PETROLEUM RECOVERY INSTITUTE

ASPHALTENE DEPOSITION DURING ENHANCED RECOVERY OF HEAVY OILS BY GAS INJECTION

FINAL REPORT SUBMITTED TO CANMET

(CONTRACT NO. 23440-8-~~9225/~~01-SQ)

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BY

S.L. KOKAL, J. NAJMAN AND S.G. SAYEGH

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CALGARY, ALBERTA

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S. L. Kokal, J. Najman and S.G. Sayegh

Petroleum Recovery Institute
Calgary, Alberta, T2L 2A6

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EXECUTIVE SUMMARY

The nature of asphaltenes and its role in the production and processing of crude oils has been the topic of numerous studies. The economics of oil production can be seriously affected by the asphaltene deposition problem. As conventional oil reserves get depleted, exploration and production trends are towards heavier oils and secondary and tertiary recovery methods. All of these will lead to a more acute asphaltene precipitation and deposition problem.

This report gives a comprehensive review of the important factors which affect asphaltene precipitation in petroleum reservoirs and in processing facilities. It discusses the nature and characteristics of asphaltenes in the crude oil and their molecular and colloidal properties. A complete description of the asphaltene deposition problem manifestations in the reservoir, well bores and well tubings, processing and transportation equipment is presented. A review is made of the experiences of the oil industry in tackling the problem and several actual field situations are examined. Various views in the research community over the nature of asphaltenes in crude oils are discussed and the two modeling approaches are detailed. Parameters which affect asphaltene adsorption on mineral surfaces are discussed and finally, future research recommendations are made.

This report also presents a novel method to visualize *in situ* asphaltene precipitation from heavy oils with light hydrocarbon gases e.g. methane, propane, ethane/propane mixtures, and carbon dioxide at reservoir pressures and temperatures. Experimental results are reported for the effects of temperature, pressure, composition and phase behavior on the formation of asphaltene precipitates from heavy crude oils. The experimental data was used to test a thermodynamic models available in the literature in which the Flory-Huggins theory is used to model solubility of the asphaltenes in oil.A general scheme is outlined for identifying field conditions where asphaltene precipitation occurs and recommendations are made for estimating the magnitude of the precipitation.

SOMMAIRE

La nature des asphaltines et le rôle qu'elles jouent dans la production, le traitement et le raffinage du pétrole, ont été l'object de nombreuses études. Les facteurs économiques, qui ont trait à la production du pétrole, peuvent être grandement affectés par le problème que pose la précipitation des asphaltines. Alors que les réserves de pétrole conventionelles diminuent constamment, l'exploration et la production se portent de plus en plus sur les huiles lourdes ainsi que sur les méthodes de recupération secondaire et tertiaire. Ces changements, notés plus haut, entraineront des problemès aigües de déposition et de précipitation d'asphaltines.

Cette étude donne une revue détaillée des facteurs dominants qui affectent la précipitation des asphaltines dans les réservoirs de pétrole et les usines de traitement. L'étude se concentre sur la nature et caractéristiques des asphaltines dans l'huile, ainsi que leurs propriétés moléculaires et colloidales. Une description complète du problème de déposition des asphaltines dans le réservoir, puits, conduits de puits, dans la phase de traitement ainsi que l'équipement de transportation y est presentée. On a fait une revue des problèmes que l'industrie pétrolifère a rencontré, les solutions apportées ainsi que des situations vécues dans les champs de pétrole. On y discute les vues multiples de la communauté scientifique sur la nature des asphaltines et les deux approches par simulations y sont expliquées en detail. Les paramètres qui affectent l'adsorption des asphaltines sur les surfaces minérales sont discutés, et finalement, on établit la direction que la recherche devrait prendre dans le future.

Ce rapport présente une toute nouvelle méthode qui visualise, in situ, la précipitation d'asphaltines des huiles lourdes à l'aide d'hydrocarbures légers. (Example: méthane, propane, mélange éthane/propane et dioxide de carbonne). Ces précipitations sont réalisées aux conditions de pression et température typiques des réservoirs étudiés. Les résultats expérimentaux démontrent les effets que la température, pression, composition et comportement de phase peuvent avoir sur la formation de précipités d'asphaltines en provenance d'huiles lourdes. Les résultats expérimentaux furent utilisés pour vérifier la validité des modèles thermodynamiques que l'on retrouve dans la littérature, dans laquelle la théorie de Flory-Huggins est utilisée pour prédire la solubilitée des asphaltines dans l'huile. Un plan d'action, visant a identifier les conditions qui mènent à la précipitation d'asphaltines dans les champs pétrolifères, fut élaboré; aussi on y retrouve des recommendations qui ont pour but d'estimer la magnitude des precipitations.

PART-A

ASPHALTENE DEPOSITION: A LITERATURE REVIEW

CHAPTER A-1

INTRODUCTION

Miscible and immiscible flooding of heavy oil reservoirs by light hydrocarbon gases, carbon dioxide and other injection gases has the potential for enhanced recovery[1]. The flooding process however causes a number of changes in the flow and phase behavior of the reservoir fluids and can significantly alter rock properties. One such change is the precipitation of asphaltenes which can adversely affect the productivity of the reservoir during the course of oil recovery. Precipitation of asphaltenes can cause formation plugging and wettability reversal which can lead to reduced recovery efficiencies.

The nature of asphaltene precipitation and its importance in the production and processing of heavy crude oils is well recognized. The existence of asphaltenes in crude oils and their deposition inside reservoirs and well bores can cause severe problems and affect the efficiency and cost of petroleum production. Due to the combined effect of increased oil consumption and decreased conventional reserves, it appears certain that the trend in the petroleum industry in the next few decades will be towards exploration and production from heavy oil reservoirs. These reservoirs are abundant and contain most of the original oil in place.

One of the methods which may be utilized to recover heavy oils is gas injection and solvent stimulation. This technique reduces the

viscosity of heavy oil and makes it mobile and enhances oil recovery. A review of the literature on phase equilibrium of light hydrocarbon gases-crude oil systems indicates that some of the recovery methods may result in the precipitation of asphaltenes from solution[2] in the crude oils. The precipitation of asphaltic material may cause plugging of the formation which in turn may lead to partial or complete failure of the recovery process. The extent, limitation and significance of this phenomenon will be addressed in this report.

The important parameters that affect asphaltene precipitation during gas injection are the molecular weights of the crude oil and the solvent gas, the pressure and temperature of the reservoir[3-5]. Precipitation of asphaltenes is a very complex process and it is generally followed by aggregation with the resins which produces an insoluble material in the heavy oil[6]. Due to the complex nature of asphaltenes, the precipitation phenomenon is not well understood.

Problems arising from asphaltene deposition have been reported in the literature[7] for many actual field situations. Some of these are the Ventura filed in California[8], Hassi Messaoud field in Algeria[9] and heavy oil fields in Venezuela[10]. In many cases, the precipitated asphaltenes can plug up the well tubing or can be carried to the well head and downstream separators causing expensive problems. Presently the asphaltenes are removed either by mechanical cleaning, chemical cleaning or reservoir condition manipulation. The costs can be substantial and may adversely affect the economics of a producing field with asphaltene

deposition problems.

There are two differing schools of thought as to the nature of asphaltenes in solution. One school of researchers considers the asphaltenes to be dissolved in the oil in a true liquid state, and may precipitate depending on the thermodynamic conditions of temperature, pressure and composition. Thus asphaltene precipitation is considered to be a thermodynamically reversible process[4,5]. Experimental results however have been mixed.

The second school of researchers considers that the asphaltenes are solid particles which are suspended colloidally in the crude oil and stabilized by large resin molecules. This makes the deposition process irreversible and methods used for colloids are utilized to describe the phenomenon. Some of the work in this area is by Leontaritis[11] and Lichaa[10,12].

CHAPTER A-2

NATURE AND CHARACTERISTICS OF ASPHALTENES

A-2.1 Definition

The classical definition[13,14] of asphaltenes is based on the solution properties of petroleum residuum in various solvents and is shown schematically in Figure 1. Asphaltenes are complex molecules defined to be soluble in benzene and insoluble in low molecular weight n-alkanes and can be derived from petroleum, coal or shale oil. Asphaltenes are also classified by the particular paraffin used to precipitate them from the crude oil and it has been shown[14-18] that various solvents precipitate different amounts of asphaltenes. Figure 2 from Reference 13 shows the amount of asphaltenes precipitated with the carbon number of the precipitating n-alkane solvent for a typical crude oil. The amounts precipitated with n-heptane and heavier n-alkanes show very little difference indicating that the most insoluble materials are precipitated by n-heptane and heavier solvents. This is the primary reason for selecting n-heptane as the most logical solvent for obtaining the asphaltenes[19,20]. However, as the precipitating n-alkane molecule gets smaller, the amount precipitated increases sharply (Figure 2). The material precipitated also has a different composition and molecular weight from the n-heptane asphaltenes.

A typical distribution of molecular types and sizes in a petroleum residuum[17] is shown in Figure 3. The saturates, aromatics, resins (polars) and asphaltenes (SARA) fractions are not evenly distributed

from the low to the high molecular weight end of the residua. The proportion of saturates decreases as the boiling point increases, while the amount of polar aromatics increases as the boiling point increases. The end point of the vacuum distillation is 565°C (atmospheric equivalent boiling point) and the molecular weight of the heaviest distillate is 552. The heavy ends below the high-vacuum distillates is a vacuum residuum and can be fractionated with propane, n-pentane or n-heptane. The composition of each successive distillation fraction or of each solvent extract varies depending upon the degree of separation or the solvent used as shown in Figure 3. The n-heptane asphaltenes consist primarily of aromatics[13] and traces of saturates. This can be seen from Figure 3 if the trends in saturates, polar-aromatics and napthene-aromatics were continued through the asphaltene fractions.

A-2.2 Asphaltene Composition

Asphaltenes are dark brown to black friable solids[21,22] with no definite melting point. They decompose on heating leaving a carbonaceous residue. There are a number of studies[6,13,21,23-30] which report the elemental compositions of various asphaltenes. Typical elemental compositions of asphaltene fractions precipitated by n-pentane and n-heptane from different parts of the world are listed in Table 1 which has been taken from Reference (21). Elemental analysis of the asphalt are generally determined gravimetrically with carbon as CO_2, hydrogen as water and sulphur as barium sulphate. The asphaltenes whose composition is given in Table 1 were isolated by use of more than 40 volumes of n-pentane (or n-heptane) as the precipitating medium. The amounts of

carbon and hydrogen vary over a very small range: 82 ± 3 % for carbon; 8.1 ± 0.7 % for hydrogen. This indicates that the H/C ratio is also fairly constant: 1.15 ± 0.05. The constant H/C ratio suggests that asphaltenes have a definite composition.

Speight[31] tabulated the elemental compositions of 57 different asphaltenes from 8 countries and found that the proportion of heteroelements (O, S, N etc.) varied significantly: 0.3 to 4.9 % for oxygen; 0.3 to 10.3 % for sulphur; 0.6 to 3.3 % for nitrogen. These values correspond to O/C ratio of 0.003 to 0.045; S/C ratio of 0.001 to 0.049; N/C ratios of 0.007 to 0.023. Exposing the asphaltenes to atmospheric oxygen can substantially alter the oxygen content, and exposing the crude oil to elemental sulphur or sulphur-containing minerals can result in excessive sulphur intake.

From Table 1 it is also clear that the compositions of n-heptane asphaltenes are different from the composition of n-pentane asphaltenes. The H/C ratios of the n-heptane asphaltenes are lower than those of n-pentane asphaltenes which suggests a higher degree of aromaticity in the n-heptane asphaltenes. The n-heptane asphaltenes contain a higher proportion of heteroelements which is indicated by the higher N/C, O/C and S/C ratios.

As mentioned earlier, asphaltenes are viewed as the most polar and highest molecular weight fraction of asphalt. The asphaltene fractions precipitated by various normal alkane solvents are usually characterized

by two major properties: polarity and average molecular weight. Polarity of asphaltenes is due to the presence of hetero-atoms and condensed aromatic rings and is arbitrarily defined by relative adsorptive strength or by solubility. Based on solubility theory for non-electrolytes[32], Long[13] has proposed a new way of describing the asphaltenes. Figure 4, which has been taken from his paper, shows a rectangular plot of molecular weight vs. polarity for the molecular types found in petroleum residuum. The polarity scale is in definable arbitrary units, and the diagonal line shown for n-heptane is drawn so that the material, above and to the right of it, is representative of the n-heptane asphaltene fraction. In other words, less polar material of higher molecular weights and more polar materials of lower molecular weight, both precipitate as asphaltenes. By using n-pentane as the precipitating solvent, both less polar and lower molecular weight materials are included in the precipitate and consequently the amount of precipitate increases.

An extension of this analysis was also made for coal asphaltenes[13] and is shown in Figure 5. Coal liquids generally have a much lower molecular weight than the petroleum asphalt and are more polar due to the presence of oxygenated compounds. If the n-heptane line is extended into the region of coal liquids, the asphaltenes precipitated will have a lower molecular weight and higher polarity than petroleum asphaltenes. Table 2 presents a comparison of the elemental compositions of typical asphaltenes from petroleum and coal liquids. The petroleum n-heptane asphaltenes are heavier and have a higher H/C ratio than

coal-asphaltenes. Typical gel permeation chromatography (GPC) molecular weight distributions for the two types of asphaltenes are shown in Figure 6 and illustrate the higher molecular weight of petroleum asphaltenes as well as the wider molecular weight distributions. Figure 7 shows the molecular weight distributions obtained by GPC of a number of n-heptane asphaltenes from various crude oils. A wide range of molecular weights can be obtained for these asphaltenes. However, molecular association of asphaltenes can be a problem in molecular weight distribution either by GPC or by vapor pressure osmometry (VPO) and can lead to erroneously high values[23,24]. These errors can lead to major distortions in the concept of asphaltene structure.

A-2.3 Asphaltene Structure

The chemical structure of asphaltenes has been the subject of numerous investigations[31,33,34] but it has proved to be a difficult task. This is not surprising considering the very complex nature of asphaltenes. However, progress has been made and there are indications that asphaltenes consist of condensed aromatic nuclei which carry alkyl and alicyclic systems with hetero-atoms scattered throughout. Other observations suggest that with increasing molecular weight of the asphaltene fraction, both the aromaticity and the proportion of hetero-atoms increase. It has been shown[6] that the amount of asphaltenes in petroleum varies with source, depth of burial, API gravity of the crude oil, the sulphur content as well as the non-asphaltene sulphur.

A working structural model for asphaltenes has been made possible

by substantial developments of numerous analytical tools during the past twenty-five years. These include chemical analysis by oxidation, hydrogenation, halogenation, nitration etc. and physical methods including infra-red (IR), nuclear magnetic resonance (NMR), mass spectroscopy, X-ray diffraction (XRD), densitometric analysis, ultra-centrifugation, electron microscopy, vapor pressure osmometry (VPO), gel permeation chromatography (GPC) etc. The data from these studies suggests that asphaltenes are structurally condensed poly aromatic ring systems bearing alkyl side-chains.

Hypothetical structures for asphaltenes have been postulated[21,35] based on NMR and spectroscopic data and are shown in Figure 8. Asphaltenes have also been subjected to X-ray analysis to gain insight into their macro-molecular structure[33,34] (Figure 9). This method gives information about the dimension of the unit cell, such as the interlamellar distance (c/2), layer diameter (L_a), height of the unit cell (L_c) and number of lamellae (N_c) contributing to the micelle. Table 3 shows the structural parameters of asphaltene fractions, determined using XRD method, as a function of the molecular weight of the asphaltenes. It can be seen that the larger diameters, intralamellar distance, micelle height and the number of lamellae in the micelle all increase with molecular weight up to a limiting value.

Another method to describe the complex structure of asphaltenes is in terms of the micro (fine) and macro (bulk) structure of these molecules[35,36]. By using a number of physical and chemical methods for

obtaining a group of structural parameters, Yen[36] proposed a hypothetical microstructure for asphaltenes, an example of which is shown in Figure 10. It is difficult to locate each group exactly in the structure and hence the locations reported are relative. Asphaltenes are anisotropic in structure and many individually oriented clusters are suspended and randomly distributed within their lower molecular weight homologs. The individual clusters are ordered and consist of a number of planar aromatic molecules stacked in layers by π-π association. The arrangement of sheets with the zig-zag chains are shown in Figure 11. These associations can result in the production of a crystallite (A), or the zig-zag chain can orient in bundle-like fashion (B) depending on the torsional angle when the propagation of sp^3-bonded orbital takes place. These island-like stacks are termed particles (C). These particles can be further associated to micelles (D) with polar peripheral groups. There are a number of weak links (E) along the chain configuration and there are imperfections in the aromatic system with di- and tri-valent hetero-atoms such as nitrogen, oxygen and sulphur. Clusters may also be linked by folding of the chains (G) or by bridging through weak links (H). The resin (I) is a small homolog of asphaltene with a higher molecular weight. Metal (L) atoms can be a coordination centers for several clusters.

It has been suggested[21] that asphaltenes are the final condensation product of oils and that there is a close relation between asphaltenes, resins and high molecular weight polycyclic aromatic hydrocarbons. Asphaltenes and resins are highly aromatic and the degree of aromaticity

plays an important role when the resins are being adsorbed by the asphaltene particles. The high aromaticity of maltenes (de-asphalted oil) indicates good solvency for asphaltenes, and the solvent power of the maltenes is one of the most important factors in determining the physico-chemical behavior of the petroleum colloid system.

The determination of molecular weights of asphaltenes is a problem because they have a low solubility in the liquids often used for their determination. Another concern in reporting molecular weights is the adsorption of resins and the association of asphaltenes which can exist at the conditions of the method of measurement. Also, the molecular weight is a function of the method used for its determination. For example, molecular weights using the centrifuge, monomolecular film, and osmotic pressure methods are generally high while lower values are obtained with cryoscopic, viscosity and vapor pressure osmometry methods. The most prevalent technique for determining the molecular weights of asphaltenes is the VPO method. The molecular weight obtained with this method should be considered an estimate only since it is a function of the solvent and its dielectric constant. A change in the reported molecular weight will lead to a different postulated structure for the asphaltenes.

A-2.4 Asphaltenes Colloidal Properties

Asphaltenes in solution in the crude oil have been regarded by many researchers as a colloidal system[6,10,12,14,21,22,37-45]. Several investigators have observed that asphaltenes carry an intrinsic charge

that may be positive or negative depending on the oil composition. If placed in an electrical field they migrate to the oppositely charged electrode[10-12]. As mentioned earlier, there is a close relationship between asphaltenes and resins in the crude oil. There are clear indications that asphaltenes are dispersed in the crude oil due to resins. The degree of dispersion depends on the aromaticity and the chemical composition of the oil. In highly aromatic oils the asphaltenes are dispersed colloidally but in the presence of excess paraffin hydrocarbons they are coagulated and precipitated. These precipitated asphaltenes can be repeptized by the addition of aromatics.

The highly polar resins act as peptizing agents for asphaltenes and are attracted by the charged asphaltenes. They are adsorbed by asphaltenes and act as protective layer. These resins and asphaltenes together are called micelles as shown in Figure 12. This concept was first proposed by Pfeiffer and Saal[45] for bitumens and later confirmed by Ray et al.[43] for oils. These micelles are separate molecular entities[39] of the crude oil and subject to all thermodynamic changes. The addition of an adequate amount of flocculant e.g. n-pentane, causes the destruction of the micelle and may result in irreversible flocculation of asphaltenes. The onset of precipitation has been linked to the surface tension of the solvent[44] and the solvent power of the flocculant[15,32]. The colloidal nature of asphaltenes was utilized by Leontaritis[11,38] to formulate a thermodynamic-colloidal model for predicting the phase behavior of asphaltenes.

A number of studies[10,12,37,40,46] have reported that asphaltenes can be precipitated by flow through capillaries and porous media. In these experiments, high streaming potentials have been generated which disturb the stabilizing electrical forces around the micelles and as a result the particles agglomerate and precipitate. This confirms that asphaltene-resin micelles are electrically charged and thus can be precipitated by the application of an electrical potential generated due to the flow of oil through sand. Similarly, application of a counter potential may prevent precipitation of asphaltenes from crude oil flowing through a porous medium.

CHAPTER A-3

ASPHALTENE DEPOSITION PROBLEM: WHERE DOES IT OCCUR ?

Asphaltene deposition can occur during the production and processing of oils and can pose a serious problem. In many cases the deposits can be formed in the reservoir, in the well tubing and can be carried through the flow lines and into the separators and other downstream equipment. The cost of cleaning these asphaltenes from equipment can be very expensive and significantly affect the economics of a project. The asphaltene deposition process is not fully understood and it can manifest itself in many places in the field[39]. This chapter discusses some of these occurrences.

A-3.1 Inside the Reservoir:

The important parameters which affect asphaltene deposition inside a reservoir are the following[3,4,7,8,9,10,12,37-39]:

(1) Reservoir pressure

(2) Reservoir temperature

(3) Composition changes of reservoir fluids

(4) Injection fluid, and

(5) Electrokinetic effects due to streaming potential generation due to reservoir fluid flow.

Asphaltenes can deposit inside the reservoir as a result of changes in any of the factors listed above. During the course of production from a reservoir, the temperature does not change significantly. The pressure

decreases gradually due to reservoir depletion but this generally tends to inhibit asphaltene precipitation. The dominant factor which cause asphaltenes to deposit are the last three factors listed above which will now be discussed in more detail.

A-3.1.1. Composition Changes of Reservoir Fluids:

The composition of a reservoir fluid will change as a consequence of normal depletion during the primary production of the reservoir. This will result in the loss of lighter components from the oil causing a decrease in GOR and an increase in the density of the fluids. As a general rule, both these effects will *reduce* the asphaltene flocculation tendency of the reservoir fluid. This is because the gas as well as the asphaltenes compete for solvency in the crude oil and when the oil loses its light ends, more of the asphaltenes can go into solution. Consequently, as the reservoir in production ages, the pressure decreases and the oil becomes heavier and asphaltene problems should be expected to decrease.

A-3.1.2 Injection Fluids:

One of the ways by which asphaltenes will deposit inside the reservoir as a result of composition changes is by injecting a fluid into the reservoir as is done during secondary and tertiary oil recovery. In secondary oil recovery, a fluid (generally water) is injected into the reservoir for displacing oil and maintaining the reservoir pressure. The injection fluid may induce asphaltene flocculation inside the reservoir depending on its composition, pressure

and temperature inside the reservoir. The deposited asphaltenes can plug the pores and result in severe permeability reduction and formation damage. During tertiary oil recovery certain chemicals or solvents are injected into the reservoir and these alter the composition of the reservoir fluids and can lead to asphaltene precipitation.

During gas flooding a miscible fluid, e.g. propane, carbon dioxide, natural gas etc., is injected into the reservoir for displacing the residual oil left after water flooding. Miscibility of the solvent with the reservoir oil is the property which will also lead to the precipitation of asphaltenes inside the reservoir matrix and its deposition on the reservoir rock. Most of the miscible solvents have the potential for causing asphaltene flocculation. As more and more of the solvent dissolves into the crude oil, the asphaltene problem (generally speaking) will increase.

The deposition process itself is not well understood and it is difficult to quantify how much of the flocculated material will deposit in-situ. This is a flow related problem and depends on a number of factors. One must also make the distinction between flocculation and in-situ deposition. The two processes depend on different mechanisms and it is possible to have flocculation without substantial deposition inside the reservoir.

Asphaltene deposition inside the reservoir can lead to a number of other effects, an example of which is the wettability shift towards oil

wetness of the reservoir rock[47-55]. Rock wettability alterations depend upon oil composition, asphaltene content, surface mineralogy, pressure and temperature. This may have a negative effect on the ultimate oil recovery because of permeability reduction and higher residual oil saturations.

A-3.1.3 Electro Kinetic Effects:

It is generally agreed that the asphaltic material present in the crude oil is in the form of colloidally dispersed particles with an electrical charge. The central part of the asphaltene micelles consists of high molecular weight compound surrounded and peptized by resins. Experimental results[10,11,12,37,40] show that asphaltenes will flocculate out of solution when placed under the influence of an electrical field. The streaming potential generated during the flow of oil through reservoir pores or well tubing can assist in flocculating asphaltenes by electrodeposition. Streaming potential is the electrical potential generated by the movement of one phase past another.

Precipitation by the electrokinetic process depends on a number of factors[11,40] such as the velocity of the flowing reservoir fluid and its composition, the zeta potential, particle size, pressure, temperature and transport properties of the oil. Experimental evidence suggests that asphaltenes will flocculate when the resin chemical potential of an oil mixture is smaller than its critical resin chemical potential. Flocculation will occur when the particles approach each other and coagulate.

As mentioned earlier, asphaltene precipitation will occur due to the streaming potential generated by the flowing fluid in the reservoir. In general, the higher the velocity of the fluid, the higher the streaming potential generated and consequently the higher the asphaltene flocculation. Therefore the asphaltene problem will be higher near the well bores where the velocity is highest. These problems can be reduced by a proper design of well acidization and also by cleaning of the deposited asphaltenes using solvent flushes.

To reduce deposition by electrokinetic effects the velocity of the fluids in the reservoir should be kept a minimum. Large draw-downs should be avoided as these result in higher fluid velocities in the formation and wells. For asphaltenic oils, the wells should be properly cleaned after periods of shut ins or workovers. The flow rate should be kept small during the initial production stages and excessive opening of surface chokes avoided as it promotes asphaltene flocculation and deposition.

A-3.2 Well Bores and Tubing:

Perhaps the place where the asphaltene problem is most acute is in the well bores and well tubing. In many instances the asphaltene deposits plug the wells and result in production losses. To compensate for these losses the pressure is reduced at the well head until it cannot be reduced any further. Production losses lead to increased costs and well clean-ups from asphaltene deposition can adversely affect the

economics of the oil recovery project. Besides added cost, asphaltene deposition inside the wells has the potential of serious accidents. For example, the malfunction of the down hole safety valves and other valves inside the well can lead to very serious consequences. In one case[39] a blow out of the asphaltene plug resulted in the shooting of highly asphaltenic sour crude oil into the air.

Wells partly or completely plugged from asphaltene deposits are cleaned using a number of methods.

A-3.2.1 Mechanical Methods:

These methods involve mechanical scraping and cleaning of the deposits inside the wells. A common method is by wireline which is a slow and costly method particularly if the asphaltene plug is long and hard. Another technique is the drilling of the plug by hydro blasting using a coiled tubing unit. Limitation of the coiled tubing operating pressure can make this cleanup method difficult. This method has failed and the tubing ruptured as a result of operating close to the maximum pressure[56]. Another method is to apply pressure and create a differential pressure across the plug to dislodge the deposits.

A-3.2.2 Chemical Cleaning:

When mechanical removal techniques are unsuccessful or not feasible, chemical clean-up methods can be used. Numerous solvents, additives and commercial chemicals are available by many companies for dissolving deposited asphaltenes. Solvent treatment, reverse and normal

circulation with hot oil have been tried with mixed results. Hydrocarbon solvents e.g. toluene, xylene and other solvents like pyridine and carbon disulphide are effective in dissolving asphaltenes but have limited value because of their cost, safety considerations and other problems. They are also a fire and explosion hazards because of their low flash points and can also create corrosion problems. These types of cleaning methods also create handling and disposal problems. They can be a big problem especially for offshore wells where the crude oil/asphaltene/solvent solution requires careful disposal. The cleanup of the well is generally designed to suit a particular well. In many cases a chemical solvent injection (to soften the deposit) can be followed by mechanical scraping. In any case cleaning of asphaltene deposits is invariably expensive and involves solving numerous problems. The most desirable method is to undertake these clean-up operation on a regular basis to prevent complete plug-ups.

A-3.2.3 Pressure, Temperature and Flow rate manipulations:

One of the ways to prevent or reduce asphaltene deposition inside wells is to monitor the operating pressure, temperature and/or production rates to avoid conditions where asphaltenes precipitate. Some of these were discussed earlier. One method is to use insulating annular fluids to avoid excessive heat losses and maintain fluid temperatures. This method however has limited application. It is known[57] that a move towards low gas-oil ratio will reduce flocculation. Therefore the simplest and the least expensive method for controlling the deposition problem is to increase the surface choke size to reduce the dissolved

gas-oil ratio. As was discussed earlier this has the same effect as a reduction of pressure and operating in the two phase region below the bubble point of the crude.

A-3.2.4 Resinous Additives:

In some cases[58] resinous additives have been found to prevent or reduce asphaltene precipitation. This method however has not been very common and more work needs to be done before successful application can be made.

A-3.3 Processing Equipment:

The insidious asphaltene deposition problem is not only limited to the reservoir, well bore and tubing but can occur in the well head processing equipment, pipeline and downstream refining facilities. In one instance[59], 25 tonnes of asphaltenes were found inside the two main gas-oil separators in the Ula field well head production facilities. The main problem is of safety of the process control equipment. Asphaltenes in the crude oil have a tendency to deposit on all process equipment surfaces. They can plug safety devices and safety relief valves on processing equipment. When these fail to open or close when required, the consequences can be disastrous. Consequently, identification of asphaltene flocculation problem and its prediction before the design and construction of production and processing facilities is very important. If it is known *a priori* that asphaltene deposition will occur, then numerous design techniques can be used to reduce the effects of the deposition problem. This emphasizes the importance of predicting and

understanding the phase behavior of asphaltenes in crude oils.

CHAPTER A-4

ASPHALTENE DEPOSITION IN FIELD SITUATIONS

Asphaltene precipitation during oil recovery is a well known problem and occurs in many areas throughout the world. This precipitate can form a sludge and can plug well bores, pipes and processing equipment. In some cases it can also lead to closure of a particular field. Cleaning of asphaltene deposits can be very expensive and, if the problem persists, can become an important factor in the economics of oil recovery from that field. This problem has been there for many years and numerous chemical products are available for cleaning. The approach taken by the oil industry has been a remedial one and the development of the more desirable alternative of preventing the problem has lagged due in part to a lack of understanding of the mechanisms involved in the asphaltene deposition process.

A-4.1 Field Problems and Description

A-4.1.1 USA

Greeley and Ventura Fields, California

The precipitation of asphaltenes has been observed even before the introduction of gas-flooding projects during the early period of crude oil production in the Greeley field of California[37]. It was reported that asphaltic bitumen granules were observed in an oil and gas separator on a producing well. They found that the asphaltic material was deposited in the well tubing and was carried to the well head and into the processing equipment. The bottom hole pressure was higher than

the bubble point pressure of the crude oil containing the dissolved gas.

In the Ventura field in California[8] significant problems occurred during the early production stages of the wells. Deposition of asphaltenes were partly responsible for the plugging of well bores and tubing. The pay zone was at a depth of 2590 m (8500 ft) and the bottom hole temperature ranged from 100° to 155° C (212 to 310°F) while the bottom hole pressure was 58.6 MPa (8500 psi). The bubble point of the crude ranged from 24.1 (3500 psi) to 31 MPa (4500 psi). During the early production period the oil was circulated to prevent and reduce the asphaltene problem. This was thought to be beneficial because it diluted the crude oil and reduced the tendency of asphaltenes to precipitate. Numerous solvents were also tried but they were not very successful. Among the solvents used were toluene, pyridine and carbon disulphide.

The author reports that the problems at the Ventura field diminished after the bottom hole pressure decreased and fell below the bubble point pressure of the crude oil. At this time many wells were redrilled and the wells have produced free from asphaltenes problems since the early 1970's.

Little Creek Field, Mississippi

Asphaltene deposition also occurred in the well tubing in the Little Creek CO_2-flooding EOR pilot plant study in Mississippi[8]. No such problem was observed during the primary and secondary recovery history of this field. The deposition is thought to have been caused by CO_2

which in the presence of water has an acidizing effect on the reservoir. Well stimulation and acidizing fluids have a damaging effect in wells that produce asphaltenic crude oils since the acid can cause asphaltene deposition as well as well bore damage. Attempts to remove the deposited asphaltenes were often unsuccessful and in some cases permanently damaged the well. Tuttle suggested that the crude oil and the well stimulation fluids should be tested for compatibility before any well stimulation operations are conducted. In cases where asphaltenes had already precipitated, mechanical cleaning techniques were found to be the most effective.

A-4.1.2 Algeria

Hassi Messaoud Field

The Hassi Messaoud field[9] is a Cambrian sandstone at a depth of 3353 m (11000 ft) with a pay zone of approximately 1536 sq. kilometers (600 sq. miles). The initial reservoir pressure was 47 MPa (6825 psi) and the bubble point pressure varied from 14.7 to 19.3 MPa (2132 to 2800 psi)on a west-east traverse of the field. The GOR varied from 183.5 to 247.6 m^3/m^3 and the oil gravity was 42.3° API. The average composition of the Hassi Messaoud crude is given in Table 4. The crude contained 0.062 wt % asphaltenes.

Asphaltene deposits were observed in the well tubing from the early stages of production. Wells often lost 20 to 25 % of wellhead pressure in 15 to 20 days, causing considerable loss in production. To prevent these deposits a program for cleaning the tubing with a solvent was

established. The profile and volume of deposit were determined by successive gauge rings and the amount of solvent for cleaning was determined. Figure 13 shows the types of profiles of the asphaltene deposited in the well tubing. These profiles provided clues to the temperature and pressure conditions at the point of deposition and the evolution of the shape of the deposit. They observed that the point in the tubing most conducive to deposition was where the pressure was just under the bubble point. Based on these observations, Hasket and Tartera[9] estimated that the problems would be largely controlled if the wells were produced at low wellhead pressures. Application of this idea has greatly reduced the asphaltene deposition problems and the number of tubing washes required.

A-4.1.3 Venezuela

Mata-Acema and Boscan Fields

Asphaltene deposition have also caused serious problems in many areas of Venezuela. One of the fields where this problem exists is the Mata-Acema field described by Lichaa[10]. In some places the asphaltene sludges have resulted in partial or complete plugging of the well. The Mata-Acema field is a Miocene sandstone reservoir at a depth of 3505 m (11,500 ft) and a bottom hole temperature of 135°C. The average composition of the crude oil is 25 % by volume of light fraction and the rest consists of C_{7+} fraction. Other properties of the various oils from this field are given in Table 5. The asphaltene content varied from 0.4 % to 9.8 % by weight for the various Mata-Acema oils. From this table it is noted that the asphaltene content in the crude increases with an

increase in the C_{7+} fraction.

The Boscan field is an Eocene sandstone that produces heavy oil with API gravities ranging from about 9 to 12 degrees. The formation is at a depth of about 2591 m (8500 ft) and at a bottom hole temperature of about 82°C. The Boscan field is one of the largest heavy oil reservoirs of Venezuela containing about 17.2 percent of asphaltenes. Table 6 presents the properties of Boscan heavy crude oil. No asphaltene problems were observed for this crude oil.

A number of acid tests were conducted at different acid concentrations with oil samples from the Mata-Acema field. The results indicate that an appreciable percentage of the asphaltenes were precipitated from the oil upon contacting with the acid. The Boscan crude which contains the highest weight % asphaltenes however did not suffer any asphaltene precipitation problems. It was reported that when the Boscan crude was mixed with the Mata-Acema crude, it prevented the precipitation of asphaltenes from the Mata-Acema crude as well. The results indicate that the Boscan crude acts as a protective agent and as a stabilizer for the asphaltenes upon contact with acid. Other tests were also conducted which showed a permeability reduction mainly due to asphaltene deposition.

Lichaa[10] found that the resins which serve as peptizing agents for the asphaltenes were easily oxidized. This increases the crude's viscosity and provides favorable conditions for the precipitation of the

depeptized asphaltenes. Effective inhibition of asphaltene deposits in the formation appear to be possible by injecting certain peptizing agents such as the refined Boscan crude. Certain electrical deposition experiments led the author to conclude that electrical effects play an important role in the asphaltene deposition process. Thus controlling the electro deposition of the asphaltene particles can lead to the development of preventive techniques.

Lake Maracaibo

Asphaltene deposition problems were encountered in the Lake Maracaibo[57] field in Venezuela which produces more than half of Venezuelan oil. It is located in western Venezuela in the Bolivar Coastal field. There are three main producing horizons of Miocene, Eocene and Cretaceous ages. The use of standard well completion techniques resulted in costly workovers for asphaltene removal from the Cretaceous wells. The Cretaceous reservoirs lie at depths from 4000-5500 m with initial reservoir pressure as high as 86 MPa. These reservoirs are highly lenticular with 50 m of net pay distributed over 450 m of gross interval. Rock permeability ranges from 1-20 md and primary production is from cased or open-hole completions.

Initial production by solution gas drive produced 40°API crude. As exploration proceeded outward from the discovery zone, the crude became heavier (30° API) due to asphaltene accumulation. The crude oil contained 10 wt % of asphaltenes and asphaltene deposition became a serious problem. Though the asphaltenes were dissolved in the crude oil

in an undersaturated state at reservoir conditions, they could be precipitated in the well tubing where the pressure and temperature changed. The solubility of the asphaltene solids in the 30° API crude is shown in Figure 14 as a function of temperature and dissolved gas oil ratio. As the amount of dissolved gas is reduced at constant temperature, asphaltene solubility increase. The asphaltenes compete with gas for solubility in the oil phase. The less the gas present, the greater the solubility of asphaltenes in the crude oil.

Therefore to prevent asphaltenes from precipitating either the flowing well head temperature can be increased, or the dissolved gas oil ratio decreased, or both. The well head temperature can be increased by using an insulating fluid in the annular space to reduce heat loss and the gas-oil ratios can be reduced by providing chokes on the well tubing or decreasing the pressure. The problem of asphaltene precipitation was eliminated (or reduced) by manipulation of the operating conditions among them being low tubing pressure, high production rate and using insulating annular fluids to cut heat losses.

A-4.1.4 Norway

Ula Field

Operational difficulties were reported from asphaltene deposition in the well tubing and production processing facilities of the Ula reservoir[59] in the Norwegian sector of North Sea. The Ula field is situated 280 kms south west of Stavanger. The reservoir is a dip closed salt dome structure in sandstone and is located 3345 m below the sea

bed. The produced oil has an API gravity of 38.8° and a GOR of 96.2 m^3/m^3. The asphaltene content of the crude oil was 0.57 % by weight. The initial pressure of the reservoir was 48.4 MPa and the temperature is 143°C.

Asphaltenes were deposited in two producing wells down hole safety valves making it difficult to open them. The deposited asphaltenes increased the friction between the flow tube and the valve housing and prevented the valves opening with normal surface hydraulic pressures. The deposition also caused a number of problems during wireline runs, wherein the tools were damaged due to asphaltene interfering with their operation. These problems led to delays, modification of the equipment and increased costs. Twenty five tonnes of asphaltenes had also accumulated inside two main gas oil separators.

Asphaltenes were found to deposit on the well tubing where the pressure was below the bubble point of the crude. However this had very little effect on the oil production because the bottom hole pressure was high enough to overcome the restriction due to asphaltene deposition. There was a small increase in the pressure drop indicating the presence of deposits.

Laboratory and field studies were carried out to determine the point of asphaltene precipitation and to predict future trends with changes in operating conditions. Field conditions were simulated in the laboratory and the asphaltene deposition confirmed. The regimes of

asphaltene deposition were studied as a function of decreasing pressure down to pressures below the bubble point of the crude oil. The areas of the tubing affected by deposition in the field corresponded to those identified by experimental measurements in the laboratory and also by pressure and temperature modeling of the wells. The large amounts of asphaltenes in the separators were attributed to the erosion of previously deposited asphaltenes from the well tubing.

The authors also reported the results obtained when they tested a number of commercially available asphaltene dissolvers for cleaning. They found that none of the commercial dissolvers to be effective when compared to pure xylene and toluene. The commercial solvents may however still be used for safety reasons.

Laboratory experiments indicated that the asphaltenes begin to flocculate at about 3 MPa above the bubble point of the crude. Accordingly, deposition will occur over the tubing length where the pressure is about 3 MPa above the bubble point down to below the bubble point pressure. Below the bubble point pressure, no deposition was observed. Within this regime the rate of deposition reaches an equilibrium with the rate of erosion of deposited particles.

The author gives two reasons for no asphaltene deposition below the bubble point pressure of the crude oil:

(1) Below the bubble point pressure the oil flashes into two phases and the turbulence of two phase flow does not allow efficient

deposition.

(2) The solvency of the crude oil for asphaltenes increases below the bubble point due to the loss of lighter ends to the gas phase. It is possible that the precipitated asphaltenes may be redissolved prior to flocculation or aggregation into larger particles.

The authors suggest that appropriate samples should be taken during field exploration and testing and asphaltene deposition be included in the standard PVT analysis. The importance of predicting asphaltene deposition in well bores and processing equipment is even more critical when the wells are offshore because of high operating and maintenance costs.

A-4.1.5 Kuwait

In Kuwait Oil Company's exploration drilling program[56], crude oil being produced from deep reservoirs were exhibiting asphalt deposition in the well tubing. In many cases the tubing was getting completely plugged and was drastically reducing production.

Several approaches were taken to solve the deposition problem among which were (1) the use of plastic coated tubing which was not successful; (2) Well stimulation using a mixture of 15 % HCl and an organic acid which was partly successful; and (3) Chemical injection which will be tried in the future. The authors also describe a few tube cleaning techniques they used and report that mechanical scraping of the wall tubes has proved to be the most economical and practical technique

for asphaltene removal.

A-4.2 Discussion

From the foregoing descriptions of various fields with asphaltene deposition problems, it is clear that the control of asphaltene deposition can be difficult and costly in field situations. The amount of asphaltene precipitated varies from field to field and depends on the nature of crude, the nature of the injection fluid and the operating pressure and temperature. Asphaltene deposition can play an important role in the production history and economics of a reservoir.

It is clear that the approach taken by most operators is a remedial one rather than preventive. This has been partly due to the complex nature of asphaltenes and their deposition process. There is still a lack of understanding of the mechanisms involved, which has retarded the development of preventive measures. However both experimental and theoretical work has been performed and is underway around the world to determine the basic mechanisms of the deposition phenomenon. Some of the work in this area is summarized below.

The asphaltene content of crude does not play an important role in the flocculation process[10]. The Boscan crude, for example, containing 17.2 % by weight asphaltenes did not cause any asphaltene deposition problems whereas the Mata-Acema crude with much less asphaltene content had numerous problems.

A number of studies[10,12,37] have shown that electrical effects are very important in the asphaltene deposition process. A proper study of the electro deposition process can lead to the development of preventive techniques. Resins also play an important role and act as peptizing agents for the asphaltenes. The asphaltene deposition process can be controlled to a certain extent by injecting into the reservoir additives containing sufficient amount of peptizing agents.

There are differing views on what the well production pressure should be. In the Hassi Messaoud[9] field, Lake Maracaibo[57] and the Ventura field[8] in California, the asphaltene problem was reduced and controlled by producing the wells at lower well head pressures. In the Hassi Messaoud field[9], asphaltene deposition did not occur after the pressure fell below the bubble point pressure of the crude. Similarly at Lake Maracaibo, the problem was controlled by minimizing the well head flowing pressure with large surface chokes. Similarly the problems at Ventura field diminished after the bottom hole pressure fell below the bubble point of the crude. As mentioned earlier the reason for the alleviation of the problem below the bubble point could be due to two phase turbulence and the increased solvency of the crude oil for asphaltenes.

The problems at the Greeley field in California[8] are also consistent with the problems at the Hassi Messaoud, Ventura and Lake Maracaibo fields. In the Greeley field asphaltic material was being deposited in the well tubing where the pressure was in excess of the bubble point

pressure and these were carried up the tubing into the gas-oil separators. In the Ula field[59] in Norway, asphaltene were precipitating when the pressure was above the bubble point pressure. Deposition occurred over the tubing length corresponding to 3 MPa above the bubble point and up to the bubble point, when no further deposition occurred. Within this pressure range the rate of deposition reached an equilibrium with the rate of erosion of deposited particles.

In contrast to the experience at the fields described above, the experience at the Prinos project[7] has been quite different. In this field the well head flowing pressure was kept at and above 10.13 MPa to avoid asphaltene problems. The bubble point of the crude varied from 7.68 to 8.72 MPa. At the start of production, the wells were produced at pressures much lower than the bubble point of the crude and this resulted in severe asphaltene deposition problems. The experience at this field is quite different than in other fields. One reason could be that the crude oil was highly sour, containing about 40 % of H_2S.

CHAPTER A-5

MODELING ASPHALTENE PRECIPITATION

A-5.1 Nature of Asphaltene in Oil

Before one starts to develop a mathematical model for the precipitation phenomenon, one must address what the true state of asphaltenes is in the crude oil. As preceding chapters show there have been a number of studies to provide an answer to the question above. Unfortunately, there is still disagreement in the research community as to the state of asphaltenes in oil. The source of disagreement stems from the question of reversibility of asphaltene precipitation.

Reversibility of a process is necessary for the development of a thermodynamic model for phase behavior. Some researchers[4] consider the asphaltene deposition process to be reversible which implies that the solid precipitate will go back into solution if the conditions were reversed. The experimental results are somewhat mixed though the majority of the results do not support this concept. Other researchers[10,12,38,39] consider the asphaltene deposition process to be irreversible by considering the asphaltenes as solid particles which are suspended colloidally in the crude oil and stabilized by resins. Colloidal science techniques are used to describe the asphaltene deposition process[11,38]. A number of experiments on asphaltenes show that the asphaltenes carry an electrical charge and this charge plays an important role in the flocculation process. From these experiments it seems possible that by controlling the charge of these particles one can

devise asphaltene deposition prevention schemes.

From work done so far on the topic of asphaltenes, the "most probable" state of asphaltenes in the original oil can be speculated by examining the available facts[39]:

1. Asphaltene particles carry an intrinsic charge[10,12] that may be positive or negative depending on the source of the oil and these particles can migrate to the opposite electrode if placed in an external electrical field.
2. Asphaltenes are stabilized by resins which act as peptizing agents. Resins get adsorbed around the asphaltene kernels and form micelles (Figure 12). These micelles are considered separate molecular entities.
3. High streaming potentials can be generated in flow tubes and core plugs through which asphaltic oils or asphaltene containing solution flow.
4. Asphaltenes and resins have a wide range of size and molecular weight distributions and are therefore considered to exist in the oil in a polydisperse (heterogeneous) state.
5. Asphaltenes and resins associate and aggregate with each other and the degree of aggregation is dependent on the oil composition.

Based on these observations, the physical model which best fits the asphaltenes/resins/oil system is a colloidal one. The asphaltenes are believed to exist in the oil as a colloidal suspension, and are stabilized by resins adsorbed on their surface. The colloidal nature of

bitumen was first proposed by Nellesteyn[44] and a colloidal model by Pfeiffer and Saal[45] in 1940. Since then, numerous studies have confirmed the applicability of their model for asphaltenes in oil.

A-5.2 Analytical Models of Asphaltene Flocculation

Based on the assumption of reversibility, two fundamentally different approaches have been taken for the development of mathematical models for asphaltene precipitation phenomenon. One is the molecular-thermodynamic approach[4,5,61,62] and the other is the thermodynamic-colloidal approach[11,38,39,43-45].

A-5.2.1 Molecular-Thermodynamic Approach

The molecular-thermodynamic model is based on the assumption that asphaltene precipitation is a reversible process. It is contended[4] that the condition of irreversibility is based mainly on titration experiments in which asphaltenes are precipitated by the addition of a flocculant and are redissolved by the addition of a solvent. There is no firm indication for irreversibility because the addition of a solvent is not the reverse process of the addition of a flocculant. Asphaltene redissolution may also take considerable equilibration time. Assuming reversibility implies that a thermodynamic model can be used. The basic concept of a molecular model is that the asphaltenes in the oil are dissolved molecules like any other as shown in Figure 15 and the amount dissolved is a function of the thermodynamic condition of the system.

The first attempts to describe asphalt phase behavior with a

thermodynamic model was made by Fussell[61]. Using a molecular model based on the Soave-Redlich-Kwong (SRK) equation of state (EOS), Fussell used a simultaneous calculation of vapor-liquid and liquid-liquid equilibria to predict the phase behavior of a live reservoir oil studied by Shelton and Yarborough[63]. The flocculating asphaltenes were considered as a separate heavy liquid phase which was in equilibrium with a light liquid and vapor phases. This model is rather simplistic and does not describe the complex phase behavior observed during the experiments.

Another study which attempted to specifically address the asphaltene phase behavior was by Hirshberg et al.[4]. They used a combination of a vapor-liquid and a liquid-liquid model instead of a full three phase model as Fussell had done. For the vapor-liquid model, they used a compositional model based on the SRK EOS and a modified Flory-Huggins[64-66] theory for liquid-liquid equilibria. The liquid phase composition was first calculated by using the EOS and assuming no asphaltene precipitation. The liquid-liquid Flory-Huggins model was then used to calculate the amount of asphaltenes precipitated from the liquid phase assuming that this precipitation does not change the vapor-liquid equilibrium. Their model takes into account the effects of pressure, temperature and composition on the asphaltene phase behavior. The Flory-Huggins model was essentially developed for polymers and was used by Hirshberg et al. to describe the molecular behavior of asphaltenes.

There are a number of drawbacks to the Hirshberg et al.'s model and some of these were pinpointed in their paper. The modified Flory-Huggins

theory is not accurate and improvements can be made if other recent theories[67] are used to describe the bulky asphaltene molecules. Improvements can also be made by using light component/asphaltene interaction coefficients as proposed by Prausnitz[64]. Another drawback with the model is that the resins/asphaltenes interactions are not adequately described and recent studies have shown that the resins play an important role in the stabilization of asphaltenes. Finally the use of a separate V-L and L-L model for phase calculations is, at best, qualitative and improvements can be made by using a full multiphase model.

The Flory-Huggins theory is valid for the case of homogeneous chain molecules of uniform molecular weight in a uniform solvent and it is well known that molecules of asphaltenes neither consist of homogeneous chain molecules nor can the deasphalted oil and the injected fluid be considered as a single uniform solvent. Since asphaltenes as well as the deasphalted oil consist of mixtures of molecules with a continuous molecular weight distribution[26,30,68], Mansoori et al.[5] utilized the thermodynamic theory for polymer solutions consisting of a polymer with heterogeneous distribution and a solvent. They formulated a model based on the polydisperse polymer theory of Scott and Magat[69,70] instead of the Flory-Huggins theory as was done by Hirshberg et al. This model was further utilized by Kawanaka et al.[62] who used the continuous mixture techniques to calculate the asphaltene-oil phase equilibria. Whereas Hirshberg et al. considered the asphaltene phase to be a liquid, Kawanaka et al. considered it to be a solid phase and performed phase

equilibria calculations using a solid-liquid (S-L) model. Recently another study[71] for modeling of asphaltene precipitation from reservoir fluid systems was proposed along the same lines as the work of Hirshberg et al.

The molecular-thermodynamic approach to asphaltene precipitation has a number of limitations:

1. It does not take into consideration the physical model for asphaltenes in oil (described earlier) completely, e.g. it does not take into account the effect of resins on asphaltene phase behavior.
2. It treats the precipitation phenomenon as reversible which is contrary to the majority of available experimental data.

The reversibility or irreversibility of asphaltene flocculation depends on the state of asphaltene-resin micelles during precipitation[39]. When the micelles are intact after precipitation, the process can be reversed by reversing the thermodynamic state. However, most studies suggest that this is not so and the case where the resin-asphaltene micelles are intact after flocculation is during asphalt separation (not the same process as asphaltene precipitation).

A-5.2.2 Thermodynamic-Colloidal Approach

The second approach to the modeling of asphaltene flocculation process, based on colloidal nature of asphaltene particles, is the molecular-colloidal model[11,38]. The model is based on statistical

thermodynamic and colloidal science techniques. The underlying assumption is that asphaltenes exist in the oil as solid particles in colloidal suspension which are stabilized by resins adsorbed on their surface (Figure 16). The transfer of resins (which act as peptizing agents) from the asphaltene phase to the oil phase and vice-versa is responsible for the aggregation of asphaltene micelle and their flocculation. The resin outer layer of the micelle acts as a stabilizer and the short range intermolecular repulsive forces between them keeps the micelle from flocculating.

The point at which the colloidal asphaltene particles begin to precipitate is the onset of asphaltene flocculation. The size of the asphaltene micelle and the thickness of the peptizing layer at the onset depends on a number of factors[39] e.g. the nature of asphaltenes and resins, the composition of oil, and the temperature and pressure. The flocculation of asphaltene micelles depends on the solvent properties of oil at the given conditions. Leontaritis[10,11,39] describes the flocculation process as follows (Figure 17):

1. The addition of a flocculant causes thinning of the peptizing layer around the asphaltene-resin micelle.
2. The solvent power of the oil changes due to the stripping of the resin layers.
3. The oil phase becomes less polar whereas the asphaltene micelle's polarity (or tendency to flocculate) increases.
4. When the micelle is stripped of the protective resin layer deeply enough (and the solvent power of the oil lowered), the micelles

aggregate and grow in size and the onset of flocculation begins.

Since the asphaltene-resin-oil-solvent system appear to be a colloidal system with the asphaltene-resin micelles in suspension, colloidal science techniques can be used to study such systems. There are two theories that deal with the stability of colloidal dispersions: "DLVO" or the Deryagin-Landau and Verwey-Overbeck theory, and the "Steric" stabilization theory[72-73]. The DLVO theory is applicable to electrolyte systems and the stability of the system is treated in terms of the energy changes which take place when particles approach one another. It involves estimation of the free energy due to the overlap of electric double layers and the van-der-Waals energy in terms of interparticle distance. The steric stabilization theory is applicable to systems where the dispersed phase is stabilized by repulsive interactions between molecules adsorbed on the surface of the suspended particles. The colloidal asphaltene dispersions in oil are believed[39] to belong to the steric category.

The amount of resins adsorbed on the asphaltene particles is a function of the resin concentration in the oil. Changing the concentration of resins in the oil will change the amount of resins adsorbed on the asphaltene particles. When the concentration of resins is low and they do not cover the entire asphaltene particle surface, the asphaltene particles will aggregate and flocculate. It is believed that when a miscible solvent is added to a crude oil, it desorbs the resins from the asphaltene surface and consequently the asphaltene particles

aggregate, grow in size and flocculate out of suspension (Figure 17).

The thermodynamic-colloidal model of Leontaritis[10,11] utilizes an equation of state approach to perform VLE calculations for the liquid phase composition. The asphaltenes are assumed to flocculate from this phase and form an asphaltene phase. The resins are assumed to split between the oil and the asphaltene phase according to the thermodynamic equality of chemical potentials ($\Delta\mu$) at equilibrium. The chemical potential of the resins in the oil phase is calculated using the simple Flory-Huggins theory. Other more elaborate, polydisperse polymer theories[69,70] can be used to improve accuracy at the cost of additional (and often unavailable) input data.

The critical resin point is defined as the point at which the concentration of resins in the liquid phase is just enough to keep the colloidal asphaltene particles completely covered with resins and in suspension. The concentration of resins in the liquid phase at this point is the critical resin concentration. At this concentration the critical chemical potential of the resins can be calculated (from Flory-Huggins theory) which will be equal to the chemical potential of resins in the solid phase (assuming thermodynamic equilibrium). The critical resin concentration and the associated critical chemical potential of the resins can be obtained from:

(i) Adsorption experiments, and

(ii) Titration experiments with n-pentane.

Once the critical resin potential is known for a particular oil

mixture, it is compared to its actual resin chemical potential and the onset of asphaltene precipitation is determined as follows (μ represents the resin chemical potential):

1. $\left(\Delta\mu_R\right)_{actual} > \left(\Delta\mu_R\right)_{critical}$ at reservoir temperature and pressure

   In this case no asphaltene flocculation is possible.

2. $\left(\Delta\mu_R\right)_{actual} = \left(\Delta\mu_R\right)_{critical}$ at reservoir temperature and pressure

   In this case the hydrocarbon mixture is at the onset of asphaltene precipitation.

3. $\left(\Delta\mu_R\right)_{actual} < \left(\Delta\mu_R\right)_{critical}$ at reservoir temperature and pressure

   In this case flocculation is possible by electrical and/or mechanical means.

From this model one can calculate the maximum amount of solvent which will have to be added to the reservoir fluid without asphaltene flocculation.

It is assumed that the nature and size of asphaltene micelle is a function of temperature only. This assumption is valid for heavier n-alkane flocculants like n-heptane with which the maximum amount of flocculated asphaltenes is essentially constant (cf. Figure 2). However, for lighter paraffins, the nature and size of flocculated asphaltenes micelles is a function of both temperature and type of flocculant. During gas flooding the miscible injectants are generally light paraffins and as a result the model requires experimental onsets of asphaltene precipitation from the oils with these paraffins as well.

The colloidal suspension stability of asphaltenes is also influenced by the strength of the charge they carry. These electrical forces are generally small and will not affect flocculation when the system is far from the onset. However, if the system is close to the onset, it is possible to have flocculation caused exclusively by electrokinetic effects. Flow of fluids cause the generation of a streaming potential which cancel the charge on the asphaltene particles and cause them to flocculate. Leontaritis[10,11] has proposed a dynamic flow model based on the electrokinetic equations of sterically stabilized colloidal suspensions. Flocculation as a result of streaming potential due to oil flow has been considered.

A-5.3 Discussion

The selection of either the molecular-thermodynamic or the thermodynamic-colloidal model of asphaltene precipitation will lead to a fundamentally different scientific approach. The accuracy of each will depend on how accurately the physical models on which they are based reflect the real state of asphaltenes in the oil. If the asphaltenes in solution are in the molecular state, then the molecular-thermodynamic models would be considered more accurate. On the other hand, if the asphaltenes are colloidal particles dispersed in oil, then the colloidal model will predict the asphaltene phase behavior more accurately.

For these reasons it is important at this time to study and establish the true state of asphaltenes in oil than do intricate mathematical modeling which is based on unrealistic assumptions. There

is need to do basic research tuned towards the understanding of the structural and compositional behavior of asphaltenes.

CHAPTER A-6

ASPHALTENE ADSORPTION ON MINERAL SURFACES

When asphaltene flocculation occurs inside the reservoir matrix, it can be followed by its deposition or adsorption on the rock surfaces. The flocculation and deposition are two different processes and are governed by different mechanisms. When deposition occurs, it can severely reduce permeability, cause formation damage and alter wettability. While a large number of studies have been conducted on the phase behavior and flocculation aspects of asphaltenes, only a few are reported on the adsorption of asphaltenes on mineral surfaces. This has primarily been due to the difficult nature of the deposition problem and the number of variables involved.

The adsorption of asphaltenes and/or resins on the mineral surfaces has been studied mainly with respect to wettability alterations[47-55,74,75] and its impact on oil recovery. The factors which control adsorption of asphaltenes and heavy ends of petroleum on mineral surface are:

1. Chemical and structural nature of the surface mineralogy.
2. The asphaltene and resin contents of the crude oil.
3. Brine pH and composition.
4. Pressure and temperature.

Specific asphaltene/mineral interactions control the degree to which such adsorption is irreversible with respect to various organic

solvents.

A-6.1 Deposition Mechanisms

After flocculation, the asphaltenes aggregates may be brought into contact with the possible retention site on the rock surface. They either deposit at the surface or are carried away by the flowing stream. The deposition process is therefore a sequence of the following mechanism[5]:

1. The contacting of asphaltene aggregate with the rock surface.
2. The adsorption of asphaltene aggregate on the rock surface.
3. The possible breaking away of previously adsorbed asphaltene aggregates.

If there are fluid films around the rock pore surface, the possible mechanism by which the asphaltene aggregates are brought to the surface are by hydrodynamic lateral diffusion in the boundary layer and Brownian diffusion due to molecular thermal motion. Once the aggregates are brought into the immediate neighborhood of, or in contact with, the rock surface, deposition may occur due to the interaction with the solid surface or deposited asphaltenes. The van-der-Waals and electrical (electrokinetic and electrostatic) forces which are either attractive or repulsive, depending on the physico-chemical conditions, can also lead to deposition. The initial deposition is viewed as a monolayer adsorption similar to the chemisorption of gases. The heats of adsorption from solution are usually small and are comparable with the heats of solution. After a monolayer has been adsorbed, the deposit can

grow through hydrogen bonding interaction with resins[4,5,6] or association with other asphaltenes similar to polymerization. This deposition of asphaltenes on the rock surface causes wettability alteration. When large quantities of asphaltenes are deposited, it can lead to permeability reduction or complete plugging.

A-6.2 Wettability Alterations

Wettability is defined as the tendency of one fluid to spread on or adhere to a solid phase in the presence of other immiscible fluids[79]. Wettability is an important factor controlling the location, flow, and distribution of fluids in a reservoir. When the rock is water-wet, there is a tendency for water to contact the majority of the rock surface and similarly, in an oil-wet system, the rock is preferentially in contact with the rock. When the rock has no preference for either oil or water, it is defined as having intermediate wettability. Other types of wettabilities are: uniform - all areas of rock have the same wettability; fractional - different areas of rock have different wettabilities; and mixed - larger pores have different wettability than the small pores. The literature is abundant with wettability studies and a few relevant ones are in references (79) to (88).

As mentioned earlier, adsorption of asphaltenes on rocks will alter rock wettability. Clementz[75] showed that wettability could be altered by treating a Berea core with a solution of petroleum heavy ends. The wettability of the Berea core shifted from water-wet to intermediate-wet after the treatment. Cuiec[83] tried to correlate different crude oil

characteristics with the restored wettability of fluid/reservoir rock systems. Figure 18 from his paper shows the relationship between the asphaltene content in the crude oil and the wettability of the reservoir. It is clear from the figure that the asphaltene content of the crude oil from water-wet reservoirs was less than 1%. On the other hand, most of the oil-wet reservoirs contained crudes with significantly higher asphaltene contents. In the intermediate zone, crude exhibited either very high or very low asphaltene content. Cuiec's procedure to quantify wettability does not distinguish between uniform or fractional wettability. Therefore, any reservoir with a mixed wettability, which is partially water-wet, will fall in the intermediate zone along with the neutral system which has no oil-wet regions. Oil compositions before and after (oil was left in the core to age for 1.5 months at 30°C) contact with a shaly sandstone were also compared. Results showed that 95 % of the asphaltenes were retained by the porous media along with 15 % of the resins and 13 % of the low molecular weight aromatics. This amounted to approximately 10 mg organic material per gram of rock. The results also indicate that crude oil components with boiling points below 350°C are not involved in solid/crude-oil interactions. This is in agreement with the study of Campbell and Orr[89] which shows that the wettability behavior exhibited by a CO_2/crude-oil system was not observed in a CO_2/refined oil system. It was shown that wettability effects allowed CO_2 to displace crude oil more efficiently than refined oil in tertiary experiments.

The consequence of wettability on the recovery of oil are very

important. Wettability shift from water-wet for native state cores may account for the low residual oil saturations achieved at high water-alternating-gas (WAG) ratios[90]. Many studies suggest that various displacement processes will be more efficient in recovering the wetting phase. Experimental evidence[91] shows that the wetting phase could be contacted more easily and displaced completely at any saturation of the non-wetting phase, while recovery of the non-wetting phase decreased as its fractional flow decreased. The high water saturation will reduce oil recovery by miscible gas displacement in water-wet reservoirs and should have little effect in oil-wet reservoirs. Other researchers[81] have also shown that displacement efficiencies were improved with lower residual oil saturations when wettability was changed from strongly water-wet to an oil-wet condition.

Several recent studies[47-49,54] have reported wettability alterations due to CO_2 flooding. Temperature and pressure effects on the extent of CO_2-induced organic deposition were reported by Fu[49] and Monger and Fu[48]. They found that the extent of CO_2-induced deposition did not correlate strongly with any single physical or chemical property of the crude. However, they found that the deposition depended weakly on the asphaltene content of the oil. The organic (asphaltene + heavy ends) deposition was not limited by rock surface availability. This deposition made the Berea core oil-wet regardless of the initial core wettability. Similarities and distinctions between CO_2-induced flocculation and deposition were made with n-paraffin induced precipitation. The presence of brine reduced but did not eliminate the adsorption in strongly

water-wet Berea cores. This is in agreement with the findings of Collins and Melrose[52]. It has also been reported[47,48,54] that clays are important deposition sites and clay stabilization enhances organic deposition.

The effect of rock mineralogy on asphaltene adsorption isotherms have been reported by Collins and Melrose[52], Gonzales and Middea[51], and Dubey and Waxman[53]. Figure 19, which has been taken from reference (52), shows Langmuir type isotherms for asphaltene adsorption on various reservoir rock minerals. The adsorption of asphaltenes on the rock surface corresponds to a full monolayer. Various solvents have been evaluated[53] for their ability to remove adsorbed asphaltenes from Kaolin. A high degree of irreversible adsorption was observed for asphaltenes on Kaolin with respect to many solvents. The most effective solvents were CH_3Cl/CH_3OH azeotrope followed by pyridine. Toluene was not very effective in the removal of adsorbed asphaltenes.

CHAPTER A-7

CONCLUDING REMARKS

The present methods of investigation of asphaltene flocculation and deposition are only the beginning of an effort to try to develop analytical predictive techniques on the phase and transport behavior of asphaltenes. The work towards this end has been difficult due to the complex nature of the problem. Presently, there are only qualitative descriptions and hypotheses available as to the physico-chemical properties of asphaltenes. A comprehensive model that would describe the phase and transport behavior of asphaltenes in oil should take into account the wide range of size and molecular distributions of asphaltenes in oil, rock-oil-brine interactions as well as molecular and colloidal nature of asphaltenes.

To implement such a model will require a number of experimental and theoretical measurements. These experiments[5] consist of the measurements of the physico-chemical properties of the crude, resins, asphaltenes, reservoir core, injection gases and their interactions. The following will be of utmost importance:

1. Molecular weight distribution of asphaltenes, resins, crude oil by numerous techniques such as GPC, simulated distillation etc.
2. Solubility parameters of asphaltenes, resins and crude oils.
3. The onset of asphaltene deposition at different pressures and temperatures and with the use of different injection fluids.
4. Titration experiments for the amount of asphaltene deposition.

5. Measurement of the size growth of asphaltene particles after flocculation and the rate of flocculation
6. Effect of mineralogy on the rate and mount of asphaltene deposition in porous media.
7. Electrophoretic experiments to determine colloidal and adsorption properties of asphaltenes on reservoir rocks.
8. Nature of asphaltenes and resins in solution in the crude oil.
9. Importance of resins/asphaltenes interactions on the deposition problem.
10. Core-flood testing for simulating in-situ asphaltene deposition at different pressures, temperatures, rock permeabilities, injection fluids, etc.

These experiments will help us towards a more fundamental understanding of the asphaltene flocculation and adsorption phenomenon. A thorough understanding will enable the researchers to formulate an appropriate model for this process.

PART-B

ASPHALTENE DEPOSITION STUDY

CHAPTER B-1

INTRODUCTION

The parameters which affect asphaltene precipitation from reservoir crudes were discussed in the previous sections. Some of these are the composition of the crude, pressure, temperature and the properties of asphaltenes. Detailed investigations of the effects of these parameters on asphaltene precipitation have been frustrated by the complex nature of the precipitation process. Also the large number and difficult nature of the experiments involved, especially at high pressures and temperatures, hamper systematic studies. For this reason, theoretical modeling to predict asphaltene precipitation with only a limited amount of experimental data appears attractive. However, the effort to model the precipitation phenomenon itself has been impeded by the disagreement about the nature of asphaltenes in solution as was discussed in a previous chapter.

The objectives of this project include experimental tests to study the phenomenon of asphaltene precipitation from crude oils. Experimental data are presented on two Canadian crude oils: Suffield crude oil with a viscosity of 600 mPa.s and Lindbergh crude oil with a viscosity of 20,000 mPa.s @ 21°C and room pressure. A series of titration experiments were carried out to determine the solubility properties of asphaltenes in these heavy oils with several n-alkane solvents. A high pressure/high temperature micromodel flooding apparatus was also constructed to study the precipitation phenomenon visually at reservoir conditions with

various solvents typically used during gas-flooding enhanced oil recovery operations. The onset of asphaltene precipitation from the crude oils was measured with various solvent gases at different pressures and temperatures.

A thermodynamic model proposed in the literature[4] was used to describe and correlate precipitate formation. The titration data of the crude oils with various n-alkanes were used to determine the solubility properties of Suffield and Lindbergh crude oils. These results were then used to predict the onset of asphaltene precipitation with various gases at different pressures and temperatures. These data can be used to identify field conditions where precipitation may occur and may be used for estimating the magnitude of the precipitation and qualitative evaluation of the precipitation process.

This part of the report outlines the experimental procedures followed, construction of the high pressure/temperature flooding apparatus, analysis of experimental data, theory behind the model, and application of the model to predict asphaltene precipitation under field conditions.

CHAPTER B-2

EXPERIMENTAL

Two Canadian heavy oils were selected for this study: one from the Suffield field in south-eastern Alberta and the other from Lindbergh field in east-central Alberta. The properties of these heavy oils are given in Tables 7 and 8 respectively. A GC simulated distillation of the heavy oils was conducted in a gas chromatograph which provided the boiling point distributions. The results are shown in Figure 20. The oils were also analyzed by gel permeation chromatograph (GPC) for their molecular weight distributions and these are plotted in Figure 21. The n-pentane insoluble asphaltenes were also analyzed using this technique and the results are shown in Figure 22. Details of the method are provided elsewhere[92].

B-2.1 Titration Experiments

A series of titration experiments were carried out to determine the solubility properties of asphaltenes in n-alkanes. Numerous methods of filtration were tried and a simple gravity filtration was found to be most appropriate for routine analysis given the nature of oil/solvent mixtures and the asphaltene precipitation. The following procedure was used:

1. Five grams of the centrifuged heavy oil is placed in a conical flask and an appropriate volume of n-alkane is added to give the desired solvent ratio. The flask is stoppered and shaken until all the oil is dissolved. The mixture is left overnight to ensure

complete flocculation of asphaltenes.

2. The solution of n-alkane and deasphalted oil is filtered using a Whatman # 42 filter. The flask is rinsed with several small volumes of the n-alkane to ensure that all dissolved oil is transferred through the filter. If required, the filter paper is washed until the filtrate is colorless.
3. The asphaltenes on the filter paper are washed with several volumes of toluene on to a pre-weighed beaker or evaporating dish. The asphaltenes remaining in the flask are also transferred into the evaporating dish after dissolving them in toluene.
4. The toluene is then allowed to evaporate in a fume hood using rapid air flow over the solution. Once the toluene has evaporated, the asphaltenes are dried in an oven at approximately 75°C for about 4 hours. The evaporating vessel is cooled and reweighed, and the result is reported as weight percent asphaltene precipitated.

B-2.2 Asphaltene flocculation with gas:

While titration experiments with liquid n-alkanes at room conditions are easy and common, high pressure and high temperature flocculation experiments with solvent gases are more difficult and time consuming. To study the effects of temperature and pressure on asphaltene flocculation behavior, an experimental micromodel was constructed. A schematic diagram of the high pressure micromodel apparatus is shown in Figure 23. It essentially consists of a glass micromodel, high pressure and high temperature micromodel holder, transfer vessels and associated flow lines, and the photographic recording system.

B-2.2.1 Glass Micromodel

The glass micromodel consists of an etched glass plate sandwiched with another glass plate with an inlet and an outlet port for fluid entry and exit. A typical micromodel pattern is shown in Figure 24 with dimensions and ports. The depth of etch is generally between 30-40 μm. The small islands in the pattern are provided for glass support in the middle. A high contrast mask is made of the pattern and it is etched onto a piece of plate glass typically 60 mm wide and 160 mm long. The detailed procedure followed for the etching process is described elsewhere[93]. Briefly the steps involved are:

1. The glass plate is thoroughly cleaned to ensure that proper chemical bonding of the silver coating to the glass surface occurs.
2. A layer of silver is deposited on one of the glass plate's surfaces so as to provide a substrate to which the photoresist can adhere.
3. The silvered surface is coated with a layer of photoresist. This photo resist forms an acid resistant layer when it is polymerized by exposure to ultraviolet (UV) light.
4. The next step is to expose the photoresist to UV light through the mask of the micromodel flow pattern. This transfers the pattern on the mask to the photoresist layer by using UV light to polymerize the resist lying underneath the transparent areas of the mask.
5. A developing step is then carried out to remove the unpolymerized photoresist, thereby leaving the silver exposed in the areas that represent the flow paths.
6. Farmers reducing agent is then used to dissolve away the silver in

the exposed areas.

7. The exposed flow paths are then etched into the glass plate's surface using hydrofluoric acid (HF).

The inlet and outlet ports are drilled into the other glass plate using a diamond drill. The two glass plates are then sandwiched and sealed together on the sides using epoxy.

B-2.2.2 High pressure micromodel cell

The high pressure cell used for mounting the etched glass micromodel is shown in Figure 25. Similar high pressure micromodels were also used by Sayegh and Fisher[93] and Kuhlman[94]. It consists of two large steel flanges with a cavity inside to accommodate the glass micromodel. This cavity is filled with a fluid (synthetic oil) which provides the confining pressure to keep the two glass plates sealed together. The pressure rating of the cell is 35 MPa. A thermocouple is placed inside the cavity to monitor the temperature of the micromodel. It is connected to a micro-processor-based Barber-Colman proportional-integral-derivative (PID) temperature controller equipped with a relay. Four cylindrical 400 Watts heaters are embedded at 90°C spacing in the steel flanges of the micromodel cell, and are connected to the controller. The complete unit is insulated with cut-out portions on each side for light source and video recording.

B-2.2.3 Transfer vessels and flow lines

There are three ports in the glass micromodel as shown in Figure 24

and the inlet and outlet tubing circuits are made for complete flexibility in selecting the direction of flow of fluids through the micromodel. One of the ports is connected to the back pressure regulator while the other two are connected to the heavy oil reservoir and the solvent transfer vessel. These connections could be adjusted without much effort for other permutations and combinations of the respective fluids entry/exits.

The transfer vessels consist of a floating piston inside a cylinder to separate the solvent gas from the displacing fluid (water). These transfer vessels were rated at 20 MPa. The back pressure regulator is essentially a vessel filled with nitrogen at the desired back pressure and connected to the outlet line of the flow system. It also acts as a collector for the produced fluids. The volumes of the fluids used in the micromodel are very small (of the order of tens of micro liters) compared to the volume of the BPR and they do not cause an appreciable rise in the nitrogen pressure. After a certain period of time the liquids accumulated in the container are purged.

The pressures of the back pressure regulator and of the inlet and outlet ports were monitored as well as the temperature of the cell. The heavy weight of the cell as well as the use of a PID temperature controller insured steady temperatures within $\pm 1^{\circ}C$. In addition to this, the transfer vessels were also equipped with pressure gauges.

B-2.2.4 Photographic system

The high pressure cell is equipped with two viewing windows. A light source is placed on one side of the high pressure cell near the window and a video camera is positioned on the other side. A macro lens and extension tube were mounted on the camera so as to obtain magnifications between 10 and 100. The camera was connected to a time-lapse VCR and a TV monitor for recording and display. A 35 mm camera could also be installed in place of the video camera for taking photographs.

B-2.2.5 Assembly

The procedure to assemble the micromodel in the high pressure cell is as follows:

1. The glass micromodel is etched and assembled as described earlier.
2. Two inlet and an outlet port are drilled into another glass plate that has the same dimensions as the one with the flow pattern.
3. The etched plate and the unetched plate are held together with the pattern on the inside and with the inlet and outlet ports properly aligned.
4. Dow Corning Silastic 732 RTU™ sealant is then used to glue the edges of these two plates together so as to provide the initial seal when the system is pressurized.
5. The micromodel is then placed inside the high pressure cell (Figure 25) and the two flanges are bolted together. Inside the cavity, the micromodel is positioned by placers.
6. The whole assembly is placed on a special support and the insulation is mounted.

7. The thermocouple is mounted inside the thermocouple well and the heaters inserted into the heater wells. The heaters are snug-fit.
8. The external flow tubes with their special air-tight assemblies are connected to one side of the steel flange.
9. The annular cavity of the cell (where the micromodel sits) is filled with a synthetic oil and most of the trapped air is purged through a port. The cavity is then pressurized up to the desired level using a manual pump. The confining fluid pressure is always maintained at least 5 MPa above the test pressure to ensure a good seal between the etched glass plate and the unetched one.
10. The temperature controller is programmed and the cell is heated up to the desired temperature. A bleed valve with an adjustable release pressure is used to control the annular pressure while the cell is being heated.

B-2.3 Experimental procedure

The procedure to carry out flow experiments will now be described. The steps involved are:

1. The temperature of the insulated cell is set at the required value. Sufficient time is allowed for the temperature to stabilize in the model since it is placed inside a heavy metal holder. For heating the cell to high temperatures, it is advisable to go up in steps as this will avoid heater "burn-out".
2. The oil and solvent are loaded into their respective transfer vessels and their pressures raised to slightly above the test pressure. It is not necessary to heat the solvent or the heavy oil

as their volumes are very small compared to the high pressure cell, and they reach the test temperature quickly upon entry into the cell.

3. The back-pressure regulator pressure is adjusted as required by either adding or releasing nitrogen.
4. The heavy oil is loaded into the crude oil reservoir and the pressure adjusted to slightly above the test pressure. The heavy oil is loaded into the micromodel and the lines are flushed up to the back pressure regulator.
5. The lines are flushed with solvent up to the back pressure regulator but bypassing the micromodel.
6. Solvent is then introduced into the micromodel to observe its phase behavior with the crude oil and it is recorded on the time-lapse VCR. In some cases the dynamic phase behavior was studied by allowing the solvent to flow and disperse into the oil. In other cases, the oil and solvent in the micromodel were isolated and allowed to equilibrate.
7. The lines are then cleaned and any asphaltenes precipitated inside the cell are removed by flushing the lines with toluene from the transfer vessels.
8. The experiment is repeated a few times to obtain consistent results.
9. The pressure is then increased and the process repeated at the next higher pressure till the maximum pressure is reached (about 20 MPa).
10. The cycle is repeated with another solvent starting again at the

low pressure and proceeding to the maximum pressure in roughly 2.5 MPa steps.

11. The whole cycle is repeated at the next higher temperature.
12. This set is again repeated for the second oil.

CHAPTER B-3

THEORETICAL

Efforts to model the asphaltene precipitation phenomenon have been limited due in part to the complex nature and the disagreement about the characteristics of asphaltenes in oil. These were discussed in a preceding chapter on modeling asphaltene precipitation. Our experience based on the experiments performed suggest that asphaltene precipitation is reversible. One can therefore use a thermodynamic model to describe the precipitation behavior. We use here the model proposed by Hirshberg et. al.[4]. This model describes the precipitation mechanism by the Flory-Huggins theory which is commonly used in the polymer industry. The large, bulky asphaltene molecules are similar in structure and behavior to the polymer molecules and the other components in the crude oil, which are much smaller, can be viewed as a solvent phase in which the asphaltenes are dissolved and suspended.

A combination of a vapor-liquid model and a liquid-liquid model are used and illustrated in Figure 26. The Peng-Robinson equation of state (PR EOS) is used to calculate the liquid phase composition assuming no asphaltene precipitation. A liquid-liquid Flory-Huggins model is then used to calculate the amount of asphaltene precipitated from the liquid phase, assuming this precipitation does not affect the vapor-liquid equilibrium. A simplified expression for the maximum volume fraction of asphaltene soluble in oil $(\phi_a)_{max}$, was derived by Hirshberg et al.[4] based on the Flory-Huggins theory and is given by:

$$(\phi_a)_{max} = \exp\left[\frac{V_a}{V_l}\left\{1 - \frac{V_l}{V_a} - \frac{V_l}{RT}\left(\delta_a - \delta_l\right)^2\right\}\right] \qquad (1)$$

where V_l and δ_l are the solubility parameter and molar volume, respectively, of the liquid phase obtained from the VL model at the conditions of pressure and temperature. δ_a and V_a are the asphaltene solubility parameter and molar volume, respectively. This expression is obtained by assuming that the precipitated phase is pure asphaltenes. This is a rather simplified picture of the asphaltene precipitation phenomenon and involves a number of simplifying assumptions which are discussed in the original paper. The performance of the model also depends on the difference in solubility parameters between the oil and the asphaltenes.

The solubility parameter is defined as a measure of the cohesive energy density or the internal pressure exerted by the molecule within a pure fluid. Hildebrand's definition of the solubility parameter is given by:

$$\delta = \left(\frac{\Delta U^v}{V}\right)^{1/2} \qquad (2)$$

where ΔU^v is the energy change upon isothermal vaporization of one mole of liquid to the ideal gas state and V is the molar liquid volume. When two liquids possessing significantly different molecules (and consequently different solubility parameters) are mixed together, the internal pressure exerted by the liquid with a higher internal pressure (higher solubility parameter) will squeeze the molecules with the lower

internal pressure (lower solubility parameter) out of the solution, thus resulting in two immiscible phases. The difference in solubility parameters of a mixture's components provides a measure of their immiscibility in each other. For the PR EOS the solubility parameter can be easily derived to give:

$$\delta^2 = \frac{a}{2\sqrt{2}\, b\, V_l}\left(1 - \frac{T}{a}\frac{da}{dT}\right) \ln\left(\frac{z + (1 - \sqrt{2})\, B}{z + (1 + \sqrt{2})\, B}\right) \qquad (3)$$

where a and b are the EOS parameters, V_l is the molar volume and B is given by

$$B = \frac{P\, b}{R\, T} \qquad (4)$$

V_l can be calculated using the PR EOS. However the molar volumes calculated using the PR EOS are generally deviate from experimental values by about 15-20 %, and consequently the translated PR EOS[95] was used in this work.

For liquid-liquid modeling purposes the system was considered to be made up of three components: deasphalted oil + solvent, resins, and asphaltenes. As described earlier, the asphaltenes molecules are large, polar, and complex molecules. The resins are structurally similar to the asphaltene molecules and play an important role in keeping the asphaltenes in solution. The resins form micelles with the asphaltenes molecules[38].

In a crude oil the asphaltenes are dissolved or suspended. Precipitation may occur if the equilibrium is altered by changing the

pressure, temperature or the composition of the crude oil. This is especially so when lighter hydrocarbon or other light gases are added to the reservoir. The light gases possess low solubility parameters and if sufficient quantities are added, the solubility parameters of the liquid phase (de-asphalted oil) is lowered, and may lead to precipitation. Similarly, changes in pressure and temperature will also alter the solubility parameter of the oil phase and induce precipitation. As a general rule of thumb, any condition which increases the deviation in $(\delta_a - \delta_l)$ in equation (1) enhances the precipitation process. This reasoning therefore suggests that reservoir crudes which are under-saturated with respect to gas will have a higher dissolving power (since they have a higher solubility parameter) than the same crude at bubble point. Therefore if the pressure is reduced for a crude above its bubble point precipitation is likely, but this will diminish or even stop if the pressure is reduced below the bubble point pressure, because the dissolving power of the crude increases as pressure is decreased below the bubble point pressure.

There are a number of limitations to the theory presented by Hirshberg et al.[4]. As mentioned earlier, it is a very simplistic approach to a very complex problem. The Flory-Huggins theory used can be substituted by appropriate (not necessarily simple) theories like those presented in References 67, 69, 70. Work along these lines is in progress[96] at the Shell Research laboratory in Calgary. Other limitations and drawbacks to the Hirshberg[4] model are given in the original paper.

CHAPTER B-4

RESULTS

B-4.1 Titration experiments with n-alkane solvents

Titration with n-alkane solvents was carried out as described earlier and the results are presented in Tables 9 and 10 for the Suffield and Lindbergh heavy oils. The experimental data are also plotted in Figures 27 and 28 for these two heavy oils. It can be seen that above a ratio of 10 ml solvent/gm oil the precipitation is complete, and as the ratio decreases below this value the amount precipitated decreases. The onset of asphaltene precipitation with various solvents was not determined in this work due to the difficulty in obtaining these data. The onset of flocculation has been determined spectrophotometrically[15] and visually[4] for lighter oils and the dilution at onset has been seen to vary for different solvents used.

The physical nature of the precipitate varied at different dilution ratios. At the higher ratios, the precipitate was more crystalline and flocculation tended to be more rapid. The amount of asphaltenes precipitated decreases as the carbon number of the n-alkane increases. This has also been observed by many other researchers. In addition, as the carbon number of the solvent increases, and for a given solvent ratio, qualitative changes in the precipitate occurred which were similar to those which took place as solvent ratio decreased for a given solvent (i.e. the pentane precipitate is more crystalline for a given ratio).

Figure 29 shows the amount precipitated (which corresponds to the maximum at high ratios for each solvent) versus carbon number, for both oils. It can be seen that more precipitate was obtained from the Lindbergh oil than for the Suffield oil for a given solvent. It was also noted that for each solvent, the Lindbergh precipitate was more crystalline, even when precipitation was incomplete at lower ratios. Lindbergh is a heavier oil than Suffield, and has a higher asphaltene content and viscosity. As the solvent's carbon number increases, the decrease in the maximum amount precipitated is much more rapid for lower carbon number solvents. From figures 27 and 28, one can see that this is indeed the case for all solvent ratios, even when precipitation is incomplete.

Solubility parameters were calculated for the solvents used and it was found that a good linear correlation existed between them and the precipitation data. Figure 30 is a plot of solubility parameter versus maximum amount precipitated for the two oils. The figure shows that as the solubility parameter increases the amount precipitated decreases. This is in agreement with equation (1) according to which the amount of asphaltenes precipitated will increase when $(\delta_a - \delta_l)$ increases. Since these parameters are for non-polar solvents, it should be possible to obtain the amount precipitated for other solvents by calculating their solubility parameters and by extrapolation.

On a molecular level, any decrease in the amount precipitated

corresponds to an increase in the solvent's ability to penetrate the asphaltene-resin micelle and limit aggregation (i.e. increasing solvent power). Therefore, as the solvent ratio decreases for a given solvent or as the carbon number increases for a given ratio, there is an increase in the effective solvent power. Taking into consideration that the polar resins are soluble to varying degree in all n-alkanes, it is suggested that their presence in the mixture is the main cause for changes in the solvent power. As more resins are dissolved into the n-alkane (which would be the case as solvent ratio increased), asphaltene aggregation would increase and the degree of precipitation would increase as well. The qualitative changes in the nature of the precipitate could also be considered to occur due to the behavior of the resins. A change in the physical nature of an asphaltene precipitate could be attributed to a change in the degree of resin/asphaltene association. It has been suggested that a precipitate is actually a conglomerate of asphaltenes and resins and the higher the degree of resin dissolution, the closer the precipitate would come to being a pure asphaltene.

The model of Hirshberg et al.[4] was used to correlate the precipitation data obtained experimentally. Equation (1) was used to obtain the best fit value of the solubility parameter of asphaltenes. The value thus obtained along with the values of V_a used for correlation of experimental data for the two heavy oil asphaltenes are listed in Table 11. The solubility parameters of asphaltenes agrees well with other values reported in the literature[4,71]. The results obtained using the model are plotted in Figure 27 and 28 for the two oils used in this

study.

B-4.2 Flocculation with light gases

A series of experiments were carried out to measure the onset of asphaltene precipitation using various light gases under pressure and temperature conditions with the two oils. The procedure was described in the preceding chapter. The results are presented in Tables 12 and 13 for the Suffield and Lindbergh heavy oils with four solvent gases used: methane, propane, ethane/propane mixtures and carbon dioxide. These results are presented as the pressure at the onset of asphaltene precipitation (determined visually). The visual observations are also presented in the video tape that accompanies this report. The video tape also presents the phase behavior and dynamic effects on adding the solvent to the heavy oil at all temperatures. This kind of data on precipitation behavior has not been presented before.

As mentioned earlier, both the static and dynamic phase behavior of the solvent with the crude oil was observed in the high pressure micromodel. In most cases the solids (or liquid) precipitated on contact of the solvent with the heavy oil. In some cases the solids were precipitated after the mixture had been equilibrated for some time. This was especially the case at the lower temperature.

No precipitation was observed during the addition of methane for pressures up to 20 MPa at all four temperatures. This is in agreement with the observations of Hirshberg et al.[4] and Lihoreau et al.[97], and

indicates that methane strips the crude oil rather than dissolve into it. It therefore enhances asphaltene *dissolution* rather then precipitation.

Propane was the most prolific of all solvents used in precipitating solids from the heavy oils. For the Suffield heavy oil the onset of precipitation at room temperature occurred at 5 MPa. The onset pressure increased to 6 MPa at 50°C and then decreased at 75 and 100°C. At the lower temperature the precipitate formed as fine particles which agglomerated to yield dark solid aggregates. No analysis could be performed on these solid particles but other studies suggest that waxes also precipitate with propane at low temperatures (0 to 30°C). As the temperature is increased the nature of the precipitated material changed. At the highest temperature the precipitate was a dark black liquid which would be precipitated on contact of the heavy oil with the solvent. In all cases, once the precipitate had formed, it could be redissolved into the heavy oil by adding more heavy oil into the micromodel cell. This is clearly shown in the video tape which accompanies this report.

A mixture of ethane and propane (1:1 volume basis) was prepared and used as a solvent. The precipitation behavior is similar to that of propane. However the pressure at onset of asphaltene precipitation is consistently higher than that for propane at all temperatures. There is a competition between ethane and propane with ethane acting as a strippant and propane dissolving into the oil and causing precipitation.

Carbon dioxide also caused precipitation at 15 MPa for Suffield heavy oil at room temperature and this pressure increased to 17 MPa at 50°C. No precipitation could be observed at 75 and 100°C with the Suffield heavy oil up to about 20 MPa. It is anticipated that precipitation will occur beyond 20 MPa. For the Lindbergh heavy oil, the onset pressure decreased with temperature. No precipitation was observed at 22°C up to 20 MPa. The nature of the precipitate changed with temperature and from oil to oil.

B-4.2.1 Discussion

For the high pressure experiments, it was not possible (due to the small volume of the cell) to obtain quantitative measurements of the amount of solids precipitated and hence the mathematical model could not be used to correlate this data. However certain trends can be outlined. At a given temperature (for a specific oil) an increase in pressure beyond the bubble point will reduce both $(\delta_a - \delta_l)$ and V_l/V_a. Both these effects will reduce asphaltene precipitation. The maximum likelihood of asphaltene precipitation will occur at the bubble point pressure. Below the bubble point of the crude, the tendency for precipitation will decrease as the crude becomes heavier (by losing the light ends) and consequently the dissolving power of the crude increases.

Temperature can affect solubility in a number of ways. An increase in temperature affects the internal energy, ΔU^v as well as the molar volume of the liquid, and both these effects cause a decrease in the

solubility parameter of asphaltenes. A temperature increase by itself will lead to a higher tendency to precipitate. However, temperature effects are also associated with solubility effects of the solvent in the oil: solubility decreases with increasing temperature (for a given pressure) and leads to a decrease in $(\delta_a - \delta_l)$ and consequently the amount precipitated. There is therefore a competing effect of temperature and composition. This is reflected in the data presented in Tables 12 and 13. The onset pressure for propane and C_2/C_3 mixtures first increases and then decreases with temperature for the Suffield as well as Lindbergh heavy oils. The effect of temperature for CO_2 is opposite for the two oils: onset pressure increases with temperature for Suffield crude oil whereas it decreases for the Lindbergh crude oil. These relative effects depend on the asphaltene solubility parameters of the two oils.

CHAPTER B-5

CONCLUSIONS

1. A high pressure and high temperature micromodel cell has been assembled to visualize in-situ asphaltene precipitation from heavy oils using light gases such as methane, propane, ethane/propane mixtures and carbon dioxide.
2. The amount of precipitation decreases as the n-alkane carbon number of the solvent increases from 5 to 10.
3. Propane was the most prolific solvent gas in terms of the precipitation of asphaltenes from the heavy oils.
4. The asphaltene solubility parameters were estimated from titration experiments with n-alkane solvents.
5. The model of Hirshberg et al.[4] can be used to qualitatively describe the precipitation behavior.

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LIST OF SYMBOLS

a = equation of state parameter

b = equation of state parameter

B = dimensionless EOS parameter

P = pressure

R = Gas constant

T = temperature

U = internal energy

V = molar volume

z = compressibility factor

δ = solubility parameter

ϕ = volume fraction

μ = chemical potential

Subscript

a = asphaltene

l = liquid

R = resins

Superscripts

v = vapor

Source	Precipitating Medium	Composition (wt %)					Atomic Ratios			
		C	H	N	O	S	H/C	N/C	O/C	S/C
Canada	*n*-pentane	79.5	8.0	1.2	3.8	7.5	1.21	0.013	0.036	0.035
	n-heptane	78.4	7.6	1.4	4.6	8.0	1.16	0.015	0.044	0.038
Iran	*n*-pentane	83.8	7.5	1.4	2.3	5.0	1.07	0.014	0.021	0.022
	n-heptane	84.2	7.0	1.6	1.4	5.8	1.00	0.016	0.012	0.026
Iraq	*n*-pentane	81.7	7.9	0.8	1.1	8.5	1.16	0.008	0.010	0.039
	n-heptane	80.7	7.1	0.9	1.5	9.8	1.06	0.010	0.014	0.046
Kuwait	*n*-pentane	82.4	7.9	0.9	1.4	7.4	1.14	0.009	0.014	0.034
	n-heptane	82.0	7.3	1.0	1.9	7.8	1.07	0.010	0.017	0.036

Table 1: Elemental composition of asphaltene fractions precipitated by different solvents

(Reference 21)

Inspection	Coal Asphaltenes	Petroleum Asphaltenes
Carbon (wt %)	86.93	81.7
Hydrogen (wt %)	6.83	7.60
Nitrogen (wt %)	1.36	1.23
Sulfur (wt %)	1.09	7.72
Oxygen (wt %)	3.8	1.7
Vanadium (ppm)	9	1200
Nickel (ppm)	3	390
VPO, molecular weight	726	5400
H/C	0.94	1.12

Table 2: Comparison of coal and petroleum asphaltenes

(Reference 13)

Molecular Weight	Structural Parameters			
	L_a(Å)	c/2 (Å)	L_c(Å)	N_c
2694	6.0	3.81	10.7	2.8
2704	6.3	3.79	10.2	2.7
3185	7.3	3.79	11.0	2.9
4338	9.1	3.74	11.6	3.1
6427	13.9	3.65	12.5	3.4
6530	14.5	3.65	13.8	3.8
7603	14.7	3.64	13.8	3.8
8158	14.8	3.64	14.0	3.9

Table 3: Structural parameters of asphaltene fractions derived by the X-ray method

(Reference 21)

Component	Mole percent
N_2	1.80
CO_2	1.32
C_1	33.95
C_2	13.95
C_3	9.91
i-C_4	1.29
n-C_4	4.66
i-C_5	1.40
n-C_5	2.48
C_6	3.59
C_7	3.30
C_8	3.25
C_9	2.89
C_{10}	2.50
C_{11}	2.13
C_{12+}	12.38
	100.00

Table 4: Average composition of the Hassi Messaoud crude

(Reference 9)

Crude Oil Identification	API Gravity (60°/60 °F)	Asphaltene in Oil (Wt %)	C_7^+ (Vol. %)
Mata-Acema — 102	27.1	1.1	68.24
Mata-Acema — 105	28.5	1.2	69.17
Mata-Acema — 202	28.0	1.4	72.04
Mata-Acema — 207	27.1	2.0	—
Mata-Acema — 210	33.4	0.8	—
Mata-Acema — 211	24.1	3.6	74.59
Mata-Acema — 219	16.6	9.8	78.96
Mata-Acema — 221	23.1	9.0	—
Mata-Acema — 223	25.2	3.8	—
Mata-Acema — 224	23.1	1.4	—
Mata-Acema — 225	36.4	0.4	56.72
Mata-Acema — 226	21.5	5.0	77.73
Mata-Acema — 228	21.0	4.0	—
Mata-Acema — 230	20.4	6.2	—
Mata-Acema — 231	26.1	3.4	—
Mata-Acema — 235	19.4	5.4	—
Mata-Acema — 239	26.2	2.0	73.59
Mata-Acema — 245	22.3	4.3	75.61

Table 5: Some properties of various oils from Mata-Acema field in Venezuela

(Reference 10)

Gravity, API (60°/60 °F)	10.2
Sulfur, (Wt. percent)	5.5
Viscosity, (cp)	
at 85 °F	50000
180 °F	800
Vanadium, ppm	1200
Nickel, ppm	150
Asphaltenes, (Wt. percent)	17.2
Resins** (Wt. percent)	29.4
Residue at 1 Atm and 590 °F (Wt. percent)	86.7
Butane and more volatile components	0.0

*Practically it is all C_7^+
**From reference 11

Table 6: Properties of Boscan

(Reference 10)

Table 7: Properties of Suffield heavy oil

Viscosity @ 21°C and atmospheric pressure :	600 mPa.s
Density @ 21°C and atmospheric pressure :	947.4 kg/m^3
n-pentane asphaltenes :	13 wt. %
Resins:	8 wt. %

Table 8: Properties of Lindbergh heavy oil

Viscosity @ 21°C and atmospheric pressure :	20000 mPa.s
Density @ 21°C and atmospheric pressure :	968.0 kg/m^3
n-pentane asphaltenes :	21 wt. %
Resins:	8 wt. %

Table 9: Asphaltene precipitation data for Suffield heavy oil

Solvent Ratio	n-Pentane	n-Hexane	n-Heptane	n-Octane	n-Decane
3	13.8	7.3	4.6		5.4
4	11.5			5.3	
5	14.1	9.1	7.2	6.2	5.9
7	14.8	10.0	9.8	7.3	
10	14.1	10.2	9.7	7.4	6.8
15		10.8			
20	13.9				
30	14.1	11.5	9.6	8.1	7.0

Table 10: Asphaltene precipitation data for Lindbergh heavy oil

Solvent Ratio	n-Pentane	n-Hexane	n-Heptane	n-Octane	n-Decane
1.5				6.0	
2.5	18.0	10.5	3.2	7.8	6.3
3.5					10.2
5.0	21.0	13.0	4.5	9.8	10.8
7.5		14.7			8.5
10.0	22.6	16.1	5.2	11.0	
15.0			7.0	12.9	10.8
30.0	19.6	14.4		11.5	

Table 11: Correlated properties of asphaltenes

	Suffield	Lindbergh
δ_a $(MPa)^{0.5}$	21.149	20.239
V_a (n-C_5 asphaltenes) m^3/kgmol	1.10	1.20
V_a (n-C_6 asphaltenes) m^3/kgmol	1.37	1.79
V_a (n-C_7 asphaltenes) m^3/kgmol	1.57	-
V_a (n-Ca asphaltenes) m^3/kgmol	1.68	2.14
V_a (n-C_{10} asphaltenes) m^3/kgmol	1.85	2.36

Table 12: Pressures* at onset of asphaltene precipitation: Suffield oil

	25°C	50°C	75°C	100°C
Methane	← No Precipitation up to 20 MPa →			
Propane	4.0	6.0	2.5	2.0
C_2/C_3(1:1)	5.0	7.5	5.0	4.0
CO_2	15.0	17.0	>20.0	>20.0

Table 13: Pressures* at onset of asphaltene precipitation: Lindbergh oil

	25°C	50°C	75°C	100°C
Methane	← No Precipitation up to 20 MPa →			
Propane	1.0	5.0	4.0	3.0
C_2/C_3(1:1)	2.5	8.5	5.0	4.0
CO_2	>20.0	20.0	17.5	15.0

*Pressures in MPa

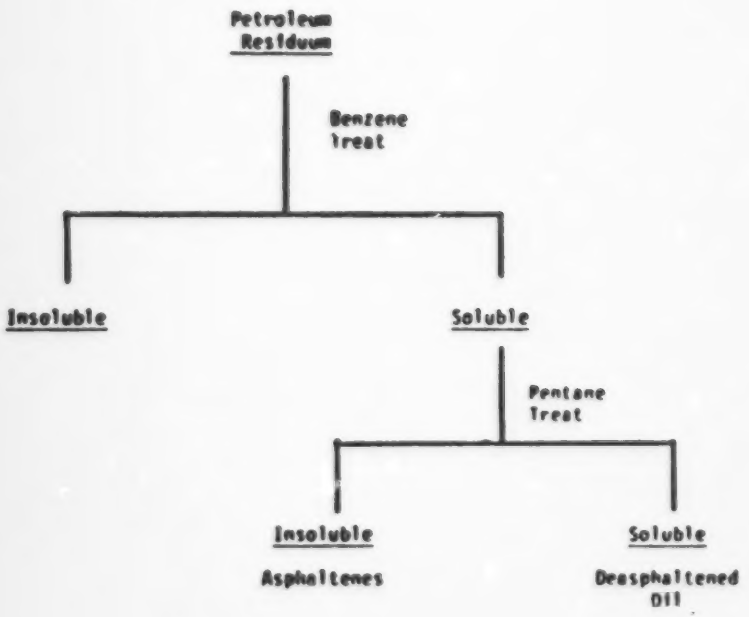


Figure 1: Separation of asphaltenes from petroleum residuum

(Reference 13)

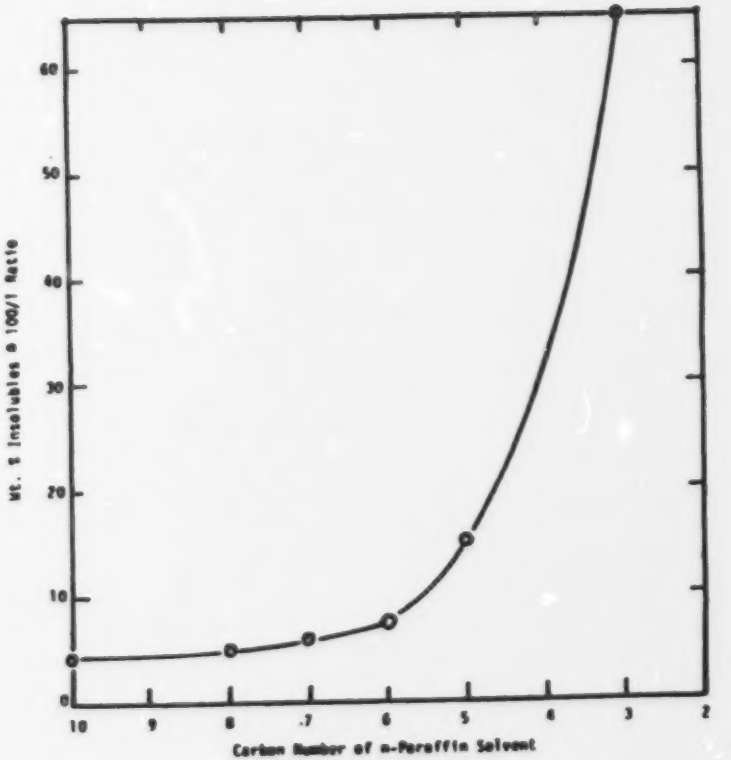


Figure 2: Effect of solvent carbon number on insolubles

(Reference 17)

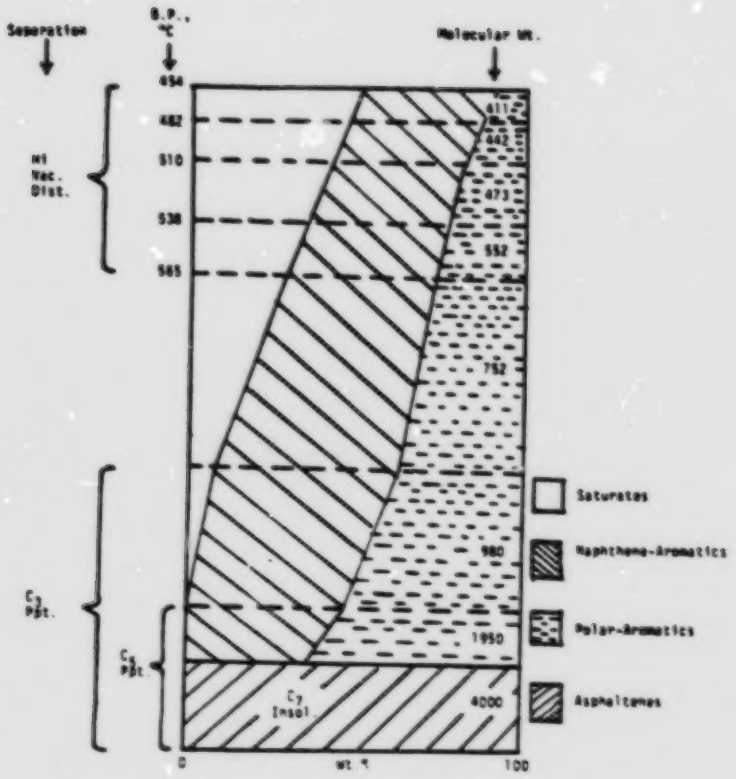


Figure 3: Distribution of molecular types and sizes in a residuum

(Reference 17)

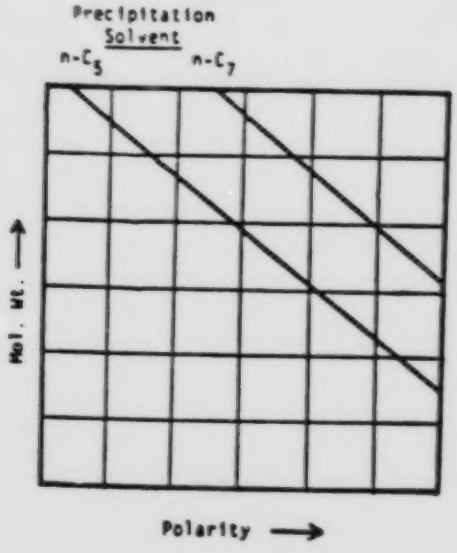


Figure 4: Petroleum asphaltene precipitation

(Reference 13)

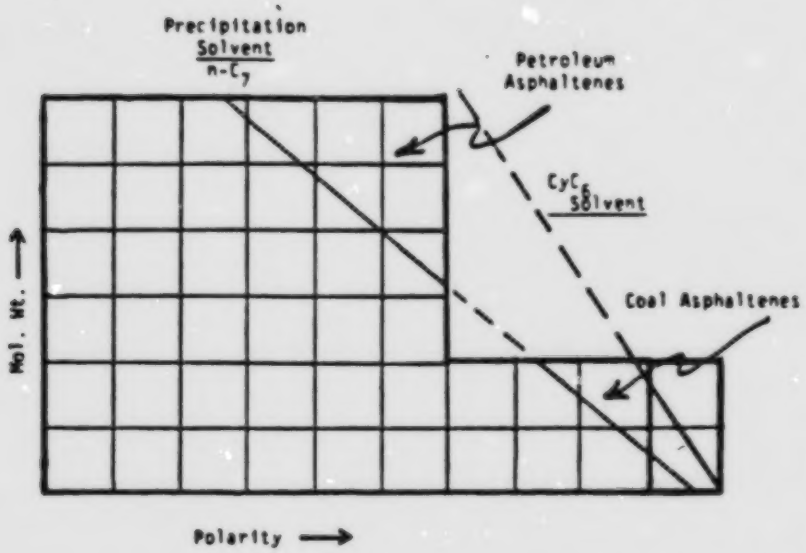


Figure 5: Comparison of petroleum and coal asphaltenes

(Reference 13)

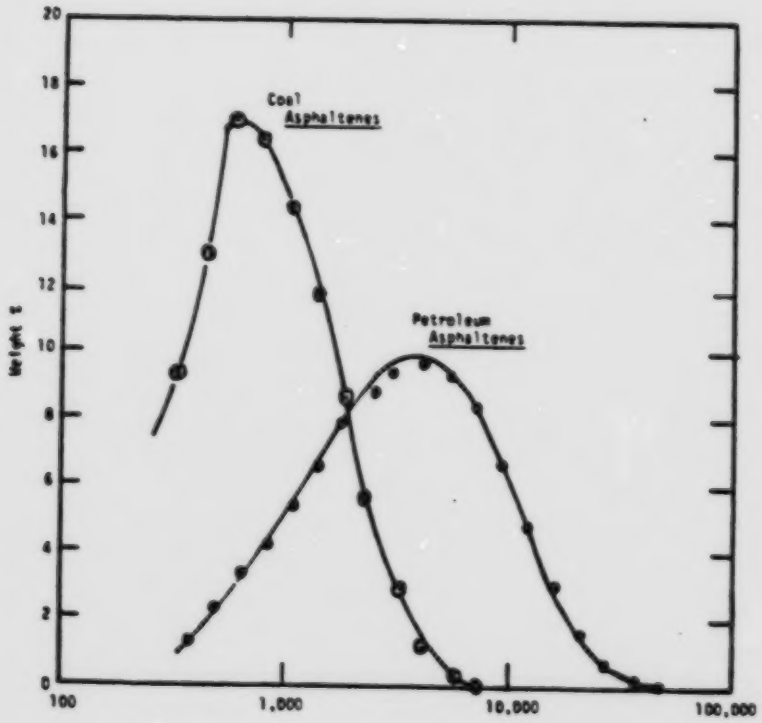


Figure 6: Comparison of molecular weight distributions of coal and petroleum asphaltenes

(Reference 13)

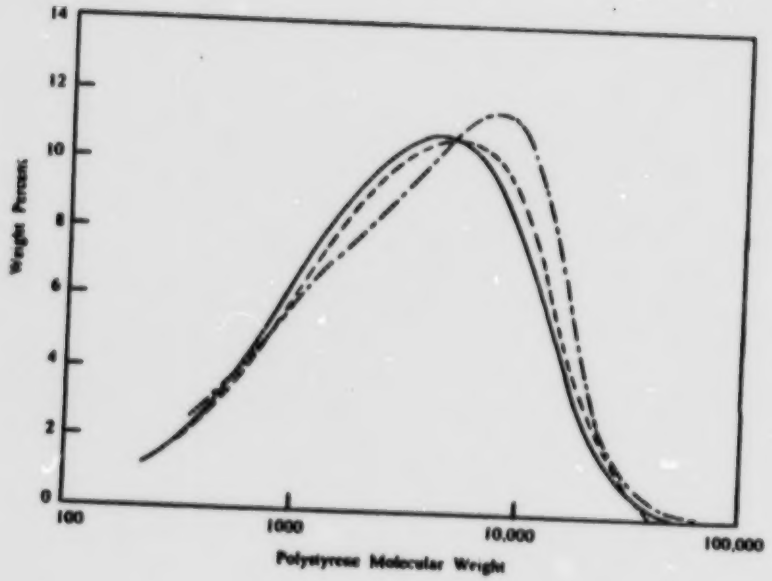


Figure 7: Comparison of n-heptane asphaltenes from various sources

(Reference 13)

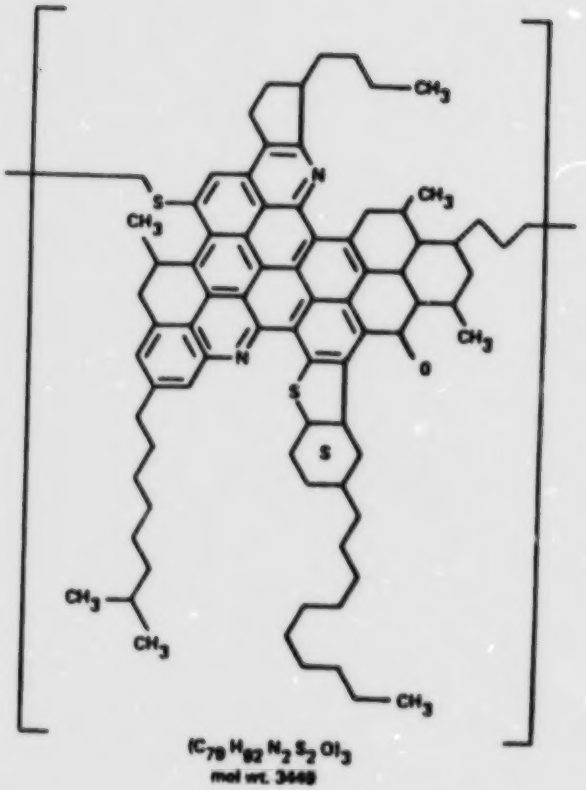


Figure 8: Hypothetical structure of a petroleum asphaltene

(Reference 21)

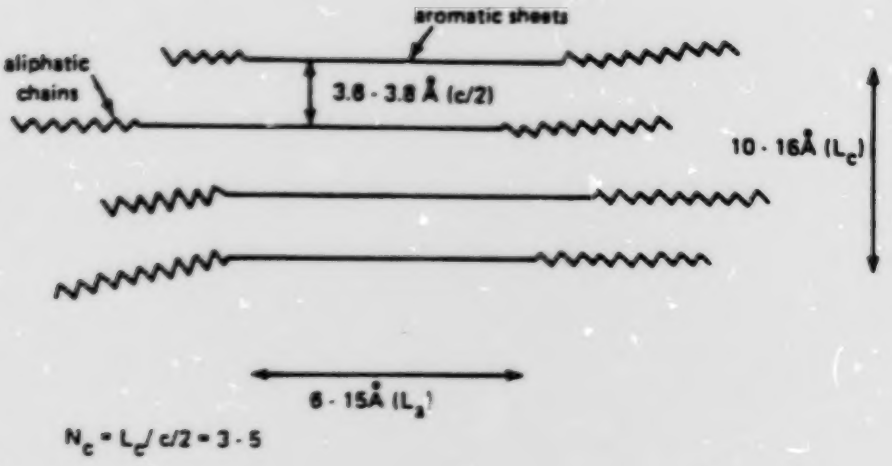


Figure 9: Representation of an asphaltene from X-ray analysis

(Reference 21)

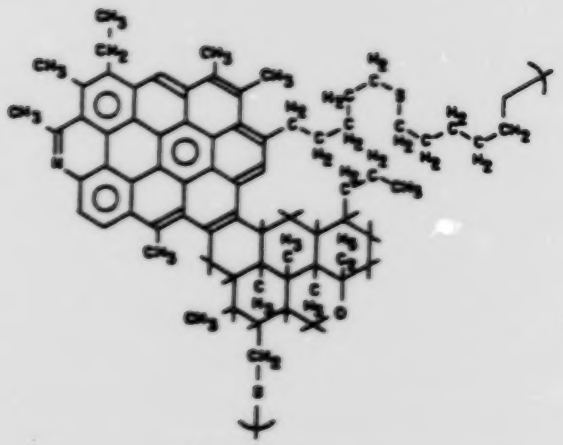


Figure 10: Hypothetical structure for a Laquinillas asphaltene

(Reference 36)

Figure 11: General features of the macrostructure of petroleum-derived asphaltenes and related substances

(Reference 36)

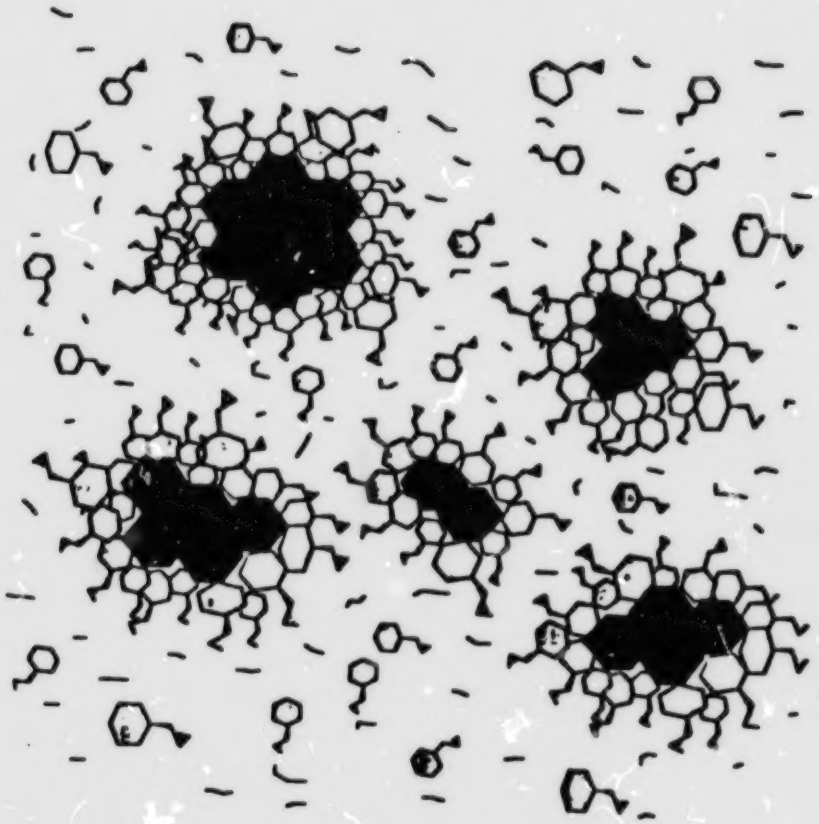


Figure 12: Peptization of asphaltenes with resins

(Reference 39)

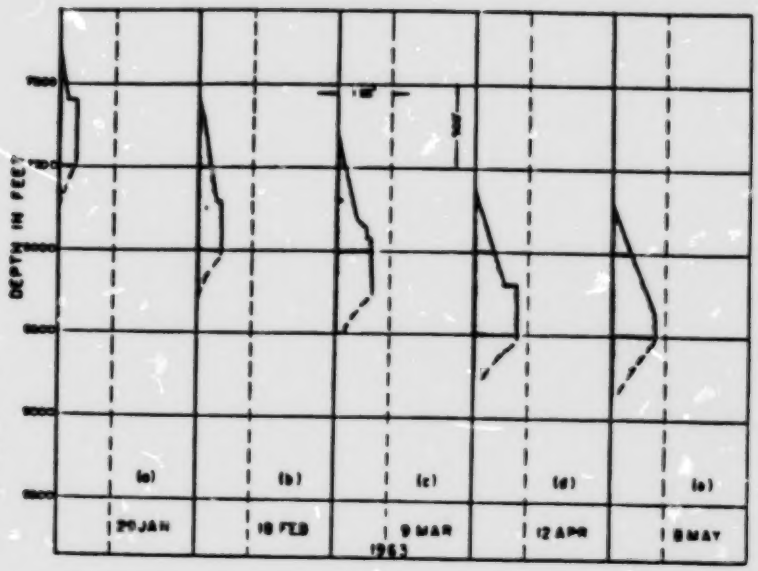


Figure 13: Types of profiles and approximate evolution of asphaltene deposits as determined by gauge rings

(Reference 9)

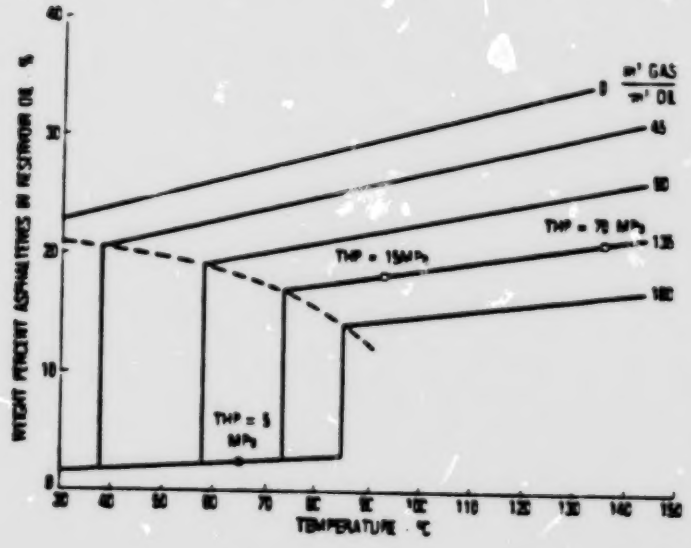


Figure 14: Asphaltene solubility in the Lake-Maracaibo (Venezuela) crude oil vs. temperature and dissolved GOR

(Reference 57)

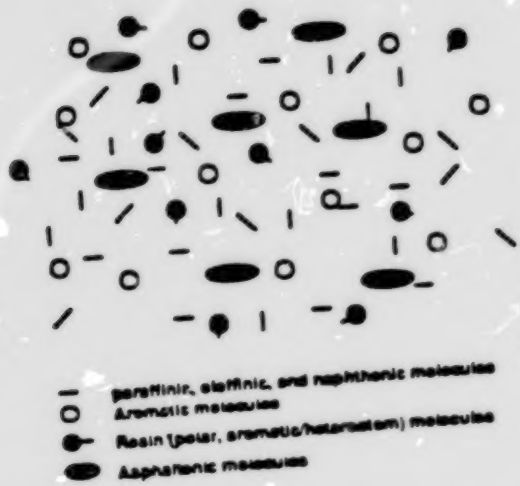


Figure 15: Molecular-Thermodynamic model

(Reference 39)

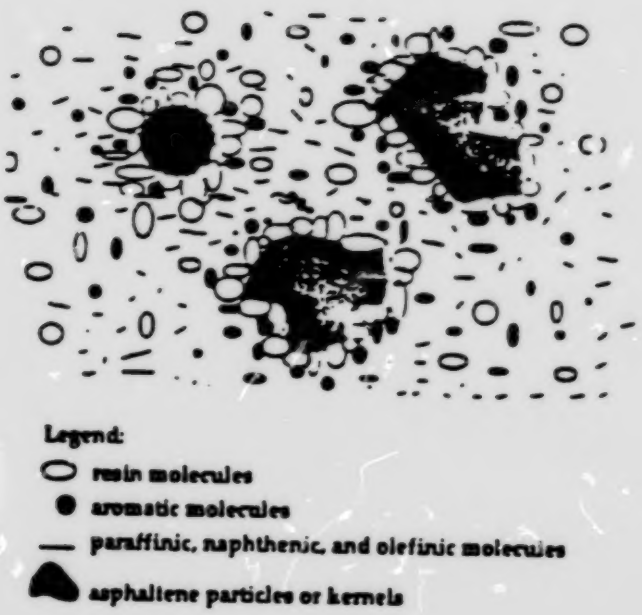


Figure 16: Thermodynamic-colloidal model

(Reference 39)

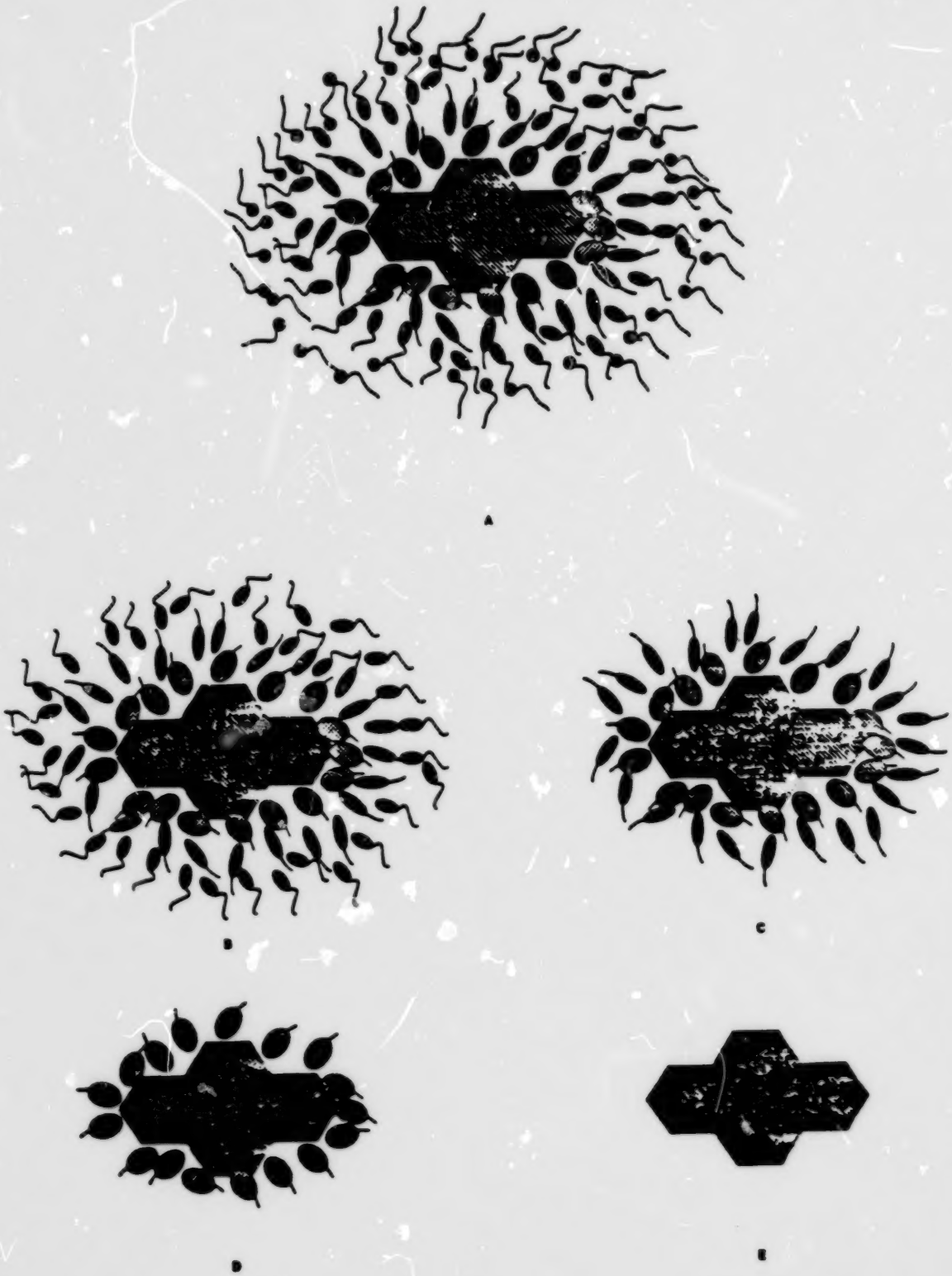


Figure 17: Asphaltene precipitation mechanism

(Reference 39)

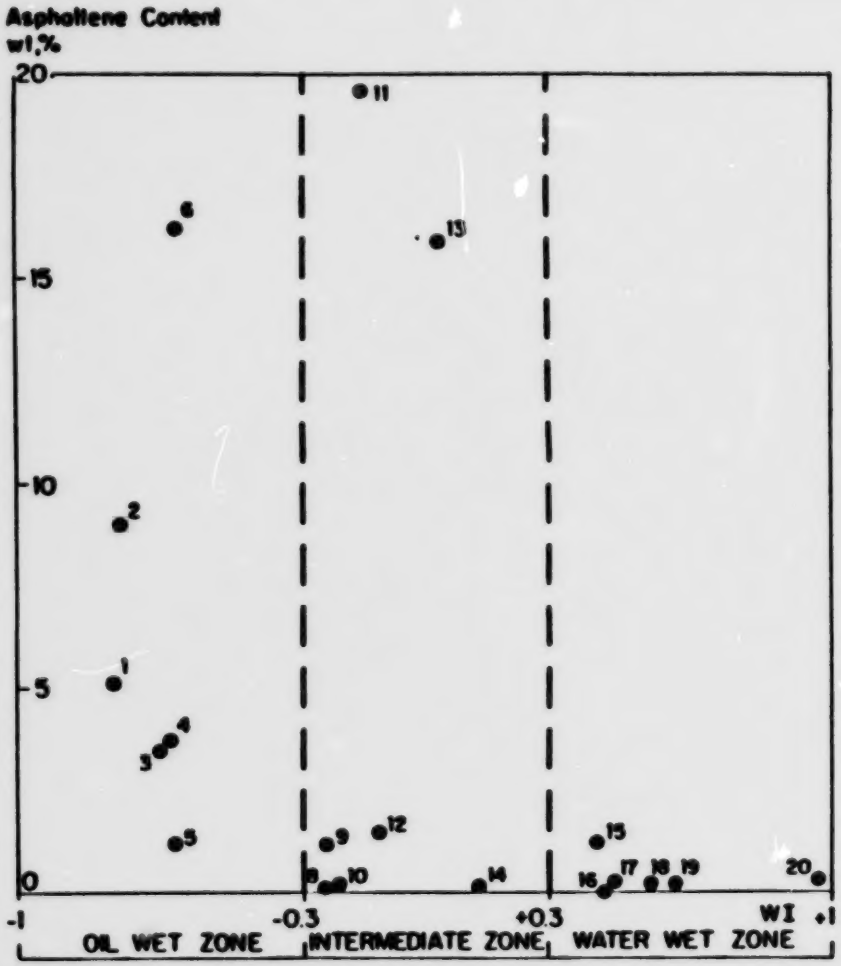


Figure 18: The wettability index-asphaltene content correlation

(Reference 83)

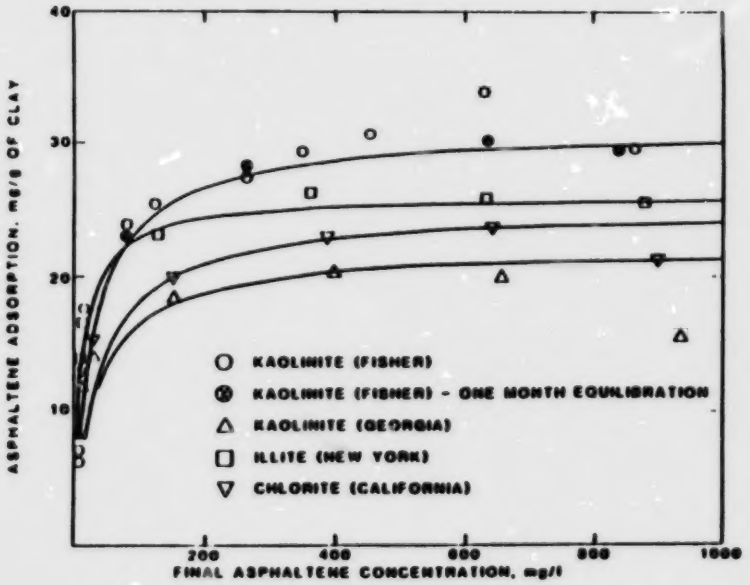
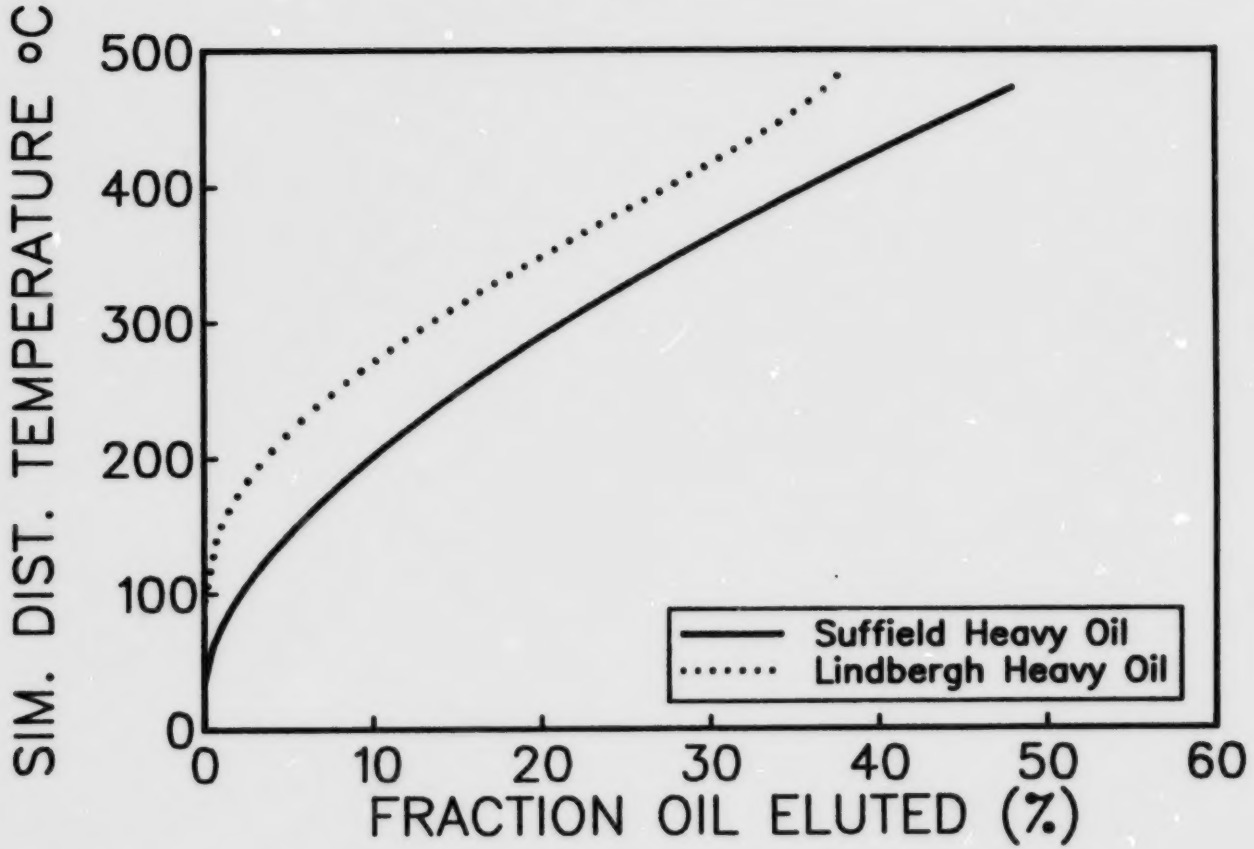


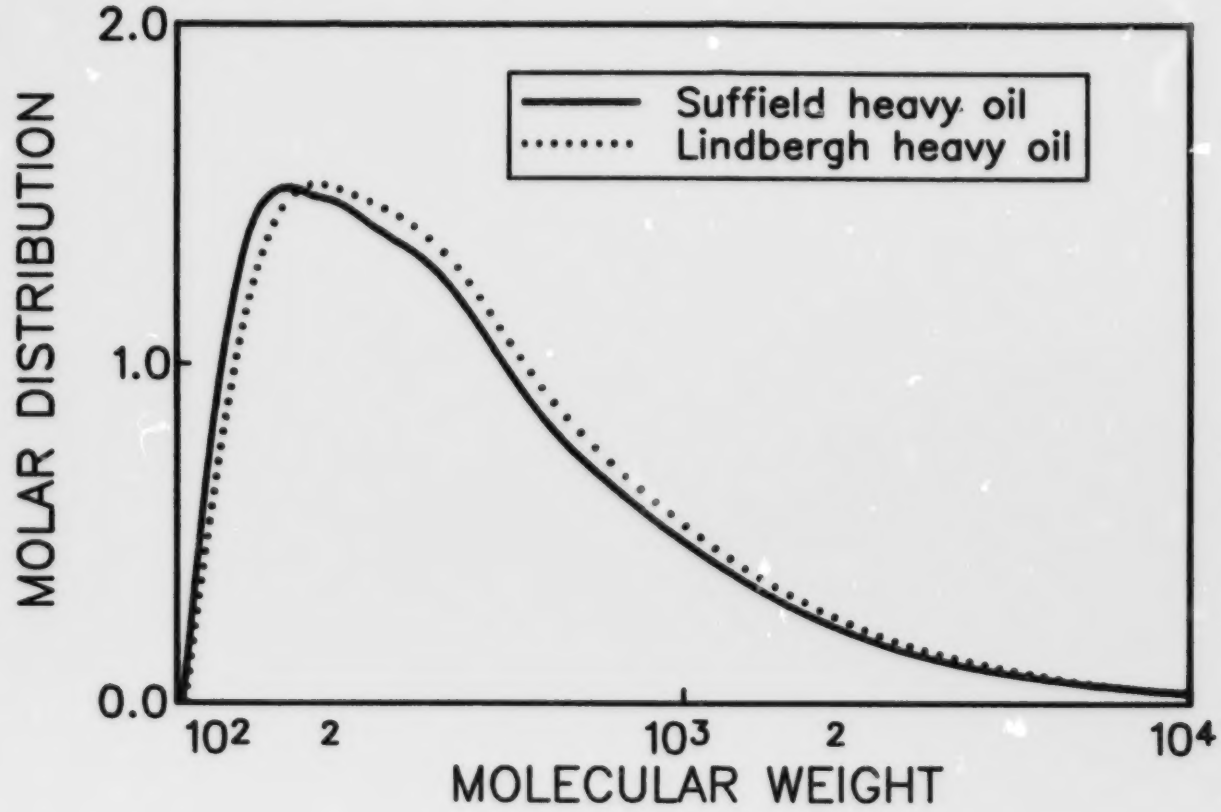
Figure 19: Adsorption of asphaltenes on various clays

(Reference 52)



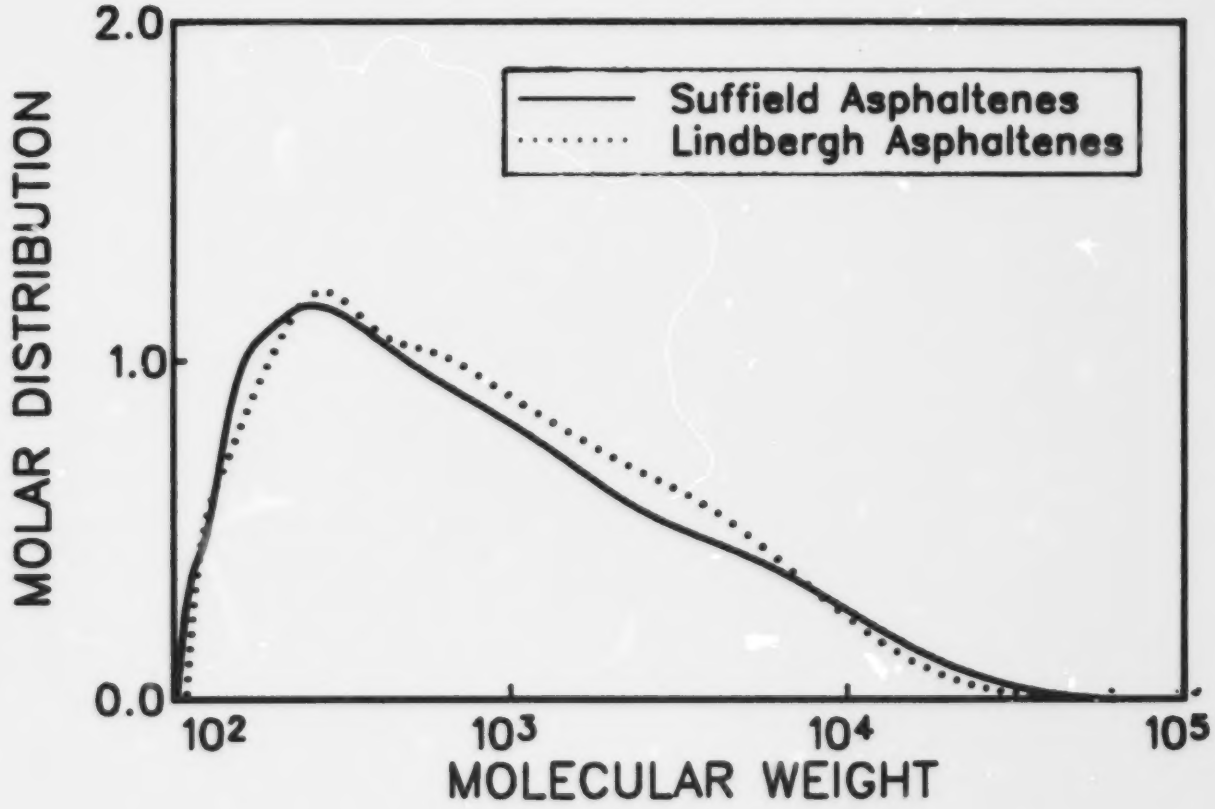
Simulated distillation of
Suffield and Lindbergh heavy oils

FIGURE 20



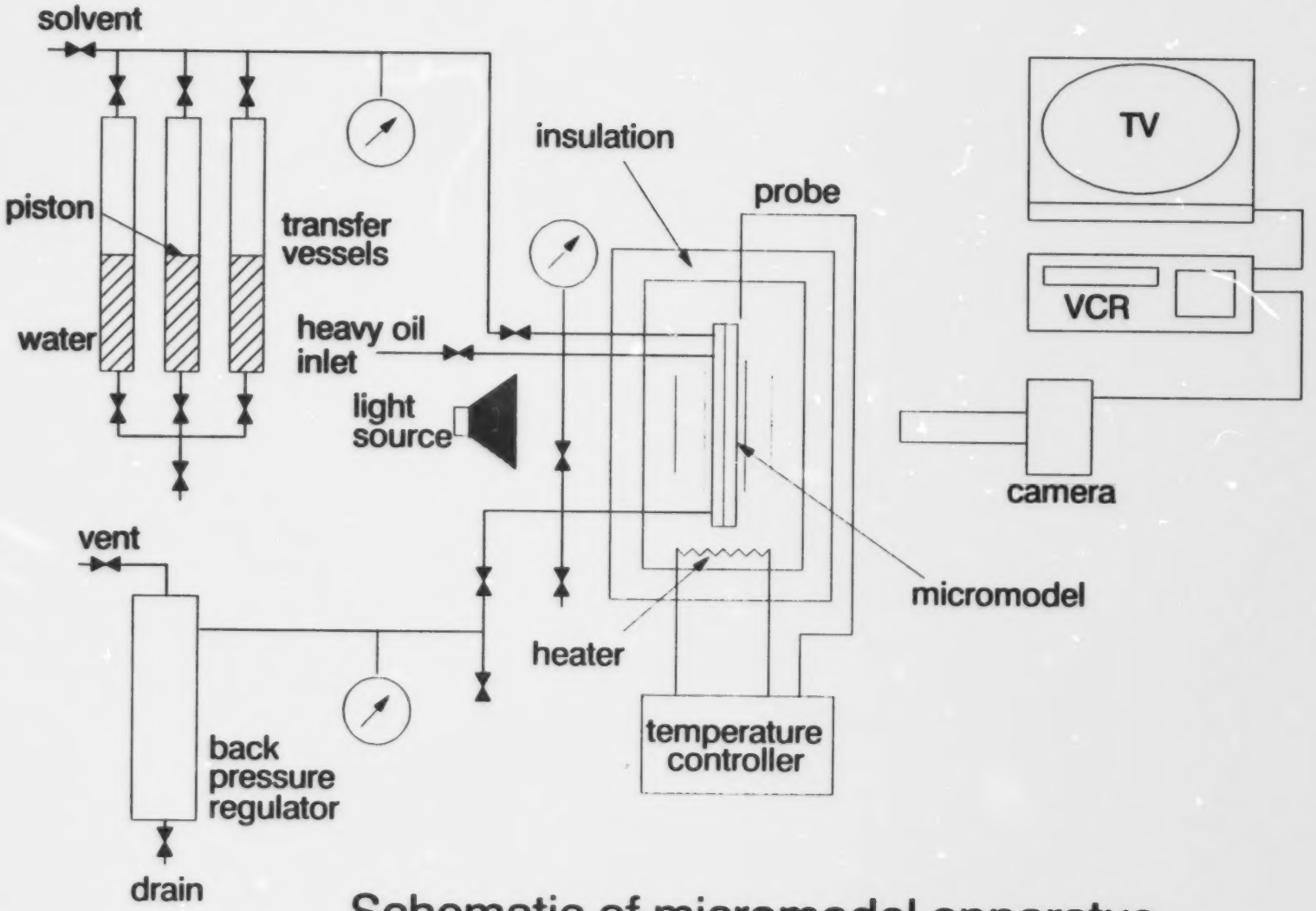
Molar distribution of Suffield and Lindbergh heavy oils

FIGURE 21



Molar distribution of Suffield and Lindbergh n–pentane insoluble asphaltenes

FIGURE 22

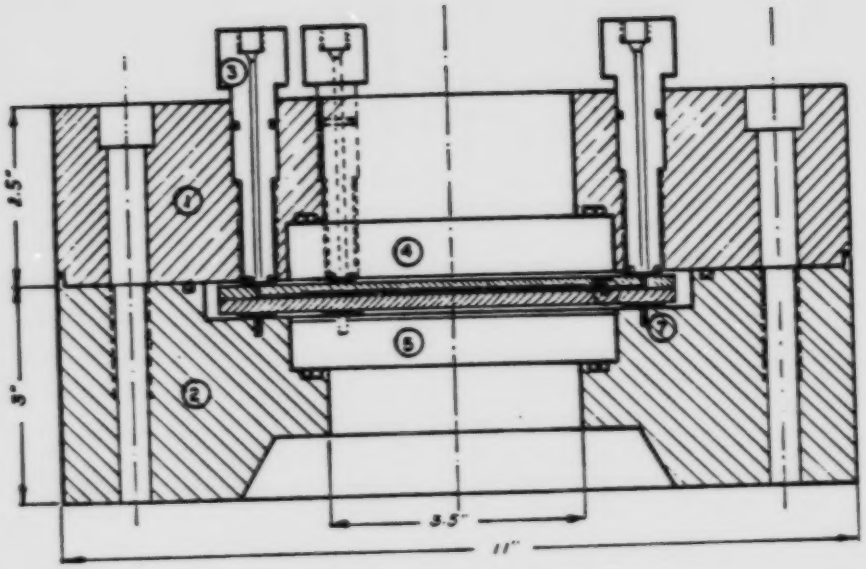


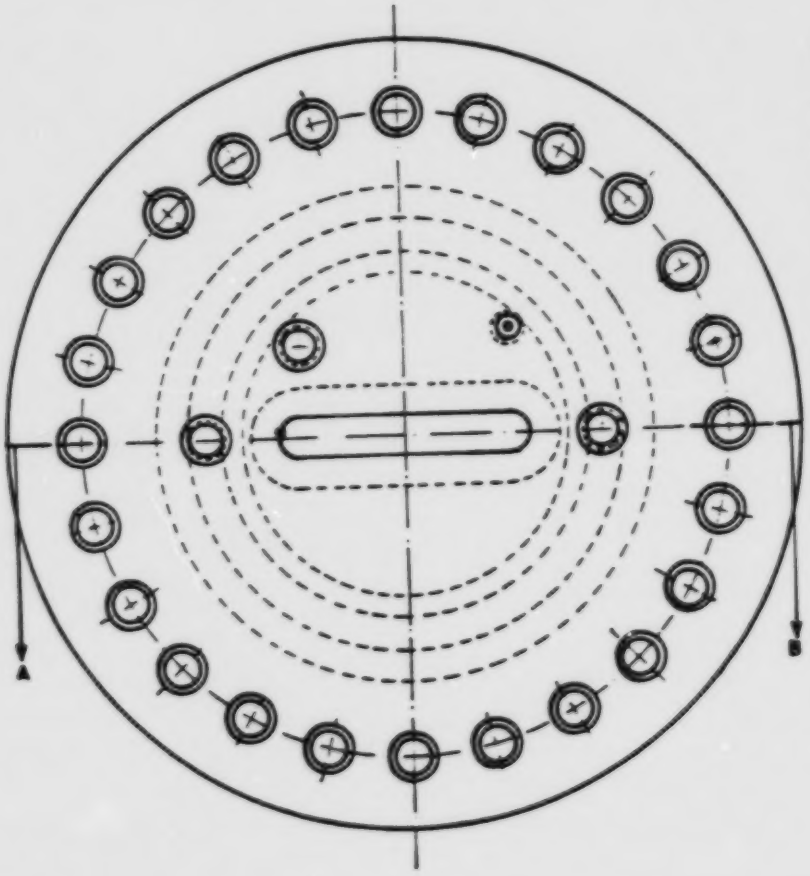
Schematic of micromodel apparatus

FIGURE 23

Glass micromodel pattern

FIGURE 24

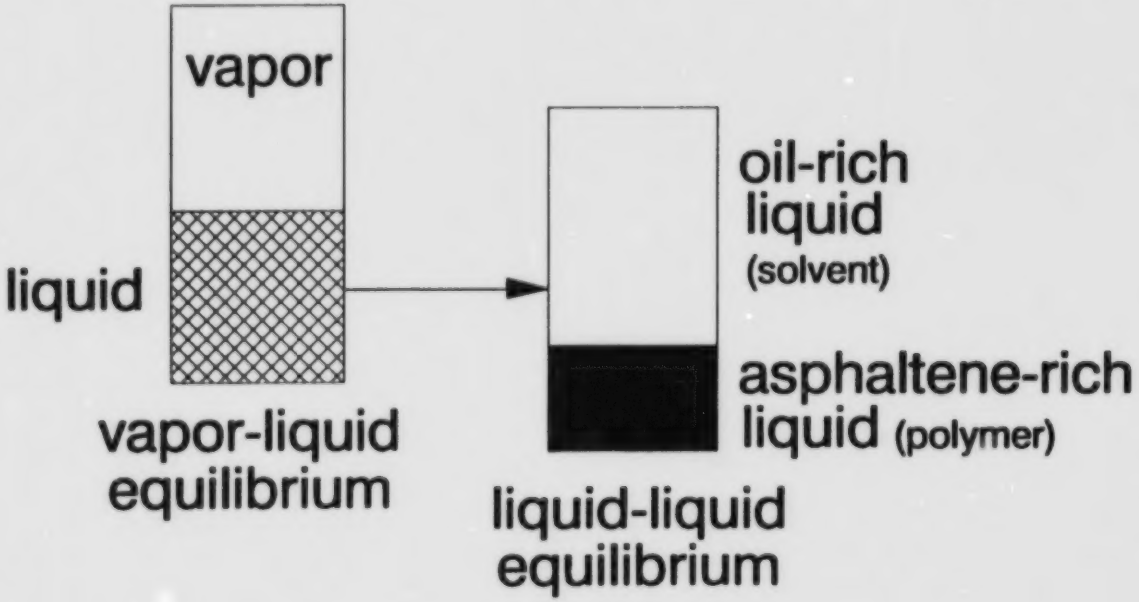




PART	DESCRIPTION
1	UPPER MAIN BODY
2	LOWER MAIN BODY
3	3-PRESSURE CONNECT.
4	UPPER SIGHT GLASS
5	LOWER SIGHT GLASS
6	GLASS MICRO MODEL
7	PRESSURE CONNECT. SUPPORT DISC (3)

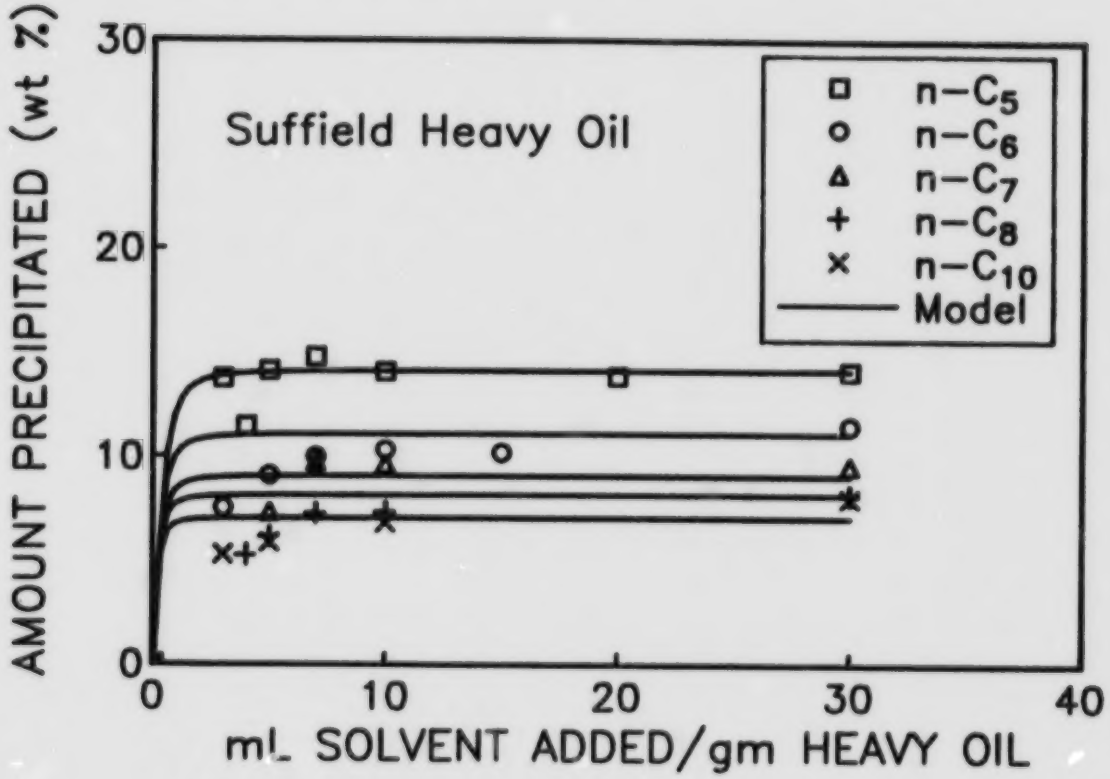
HIGH PRESSURE MICRO MODEL

FIGURE 25



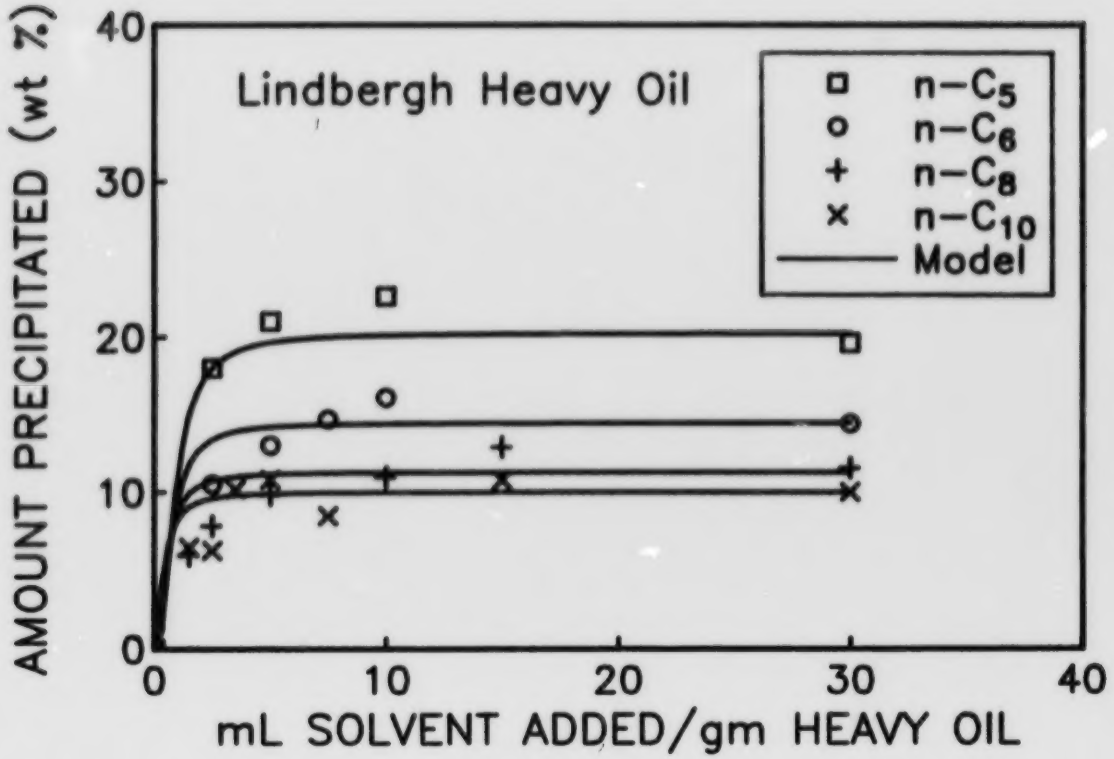
Modeling approach using
Flory-Huggins theory
(Reference 4, 71)

FIGURE 26



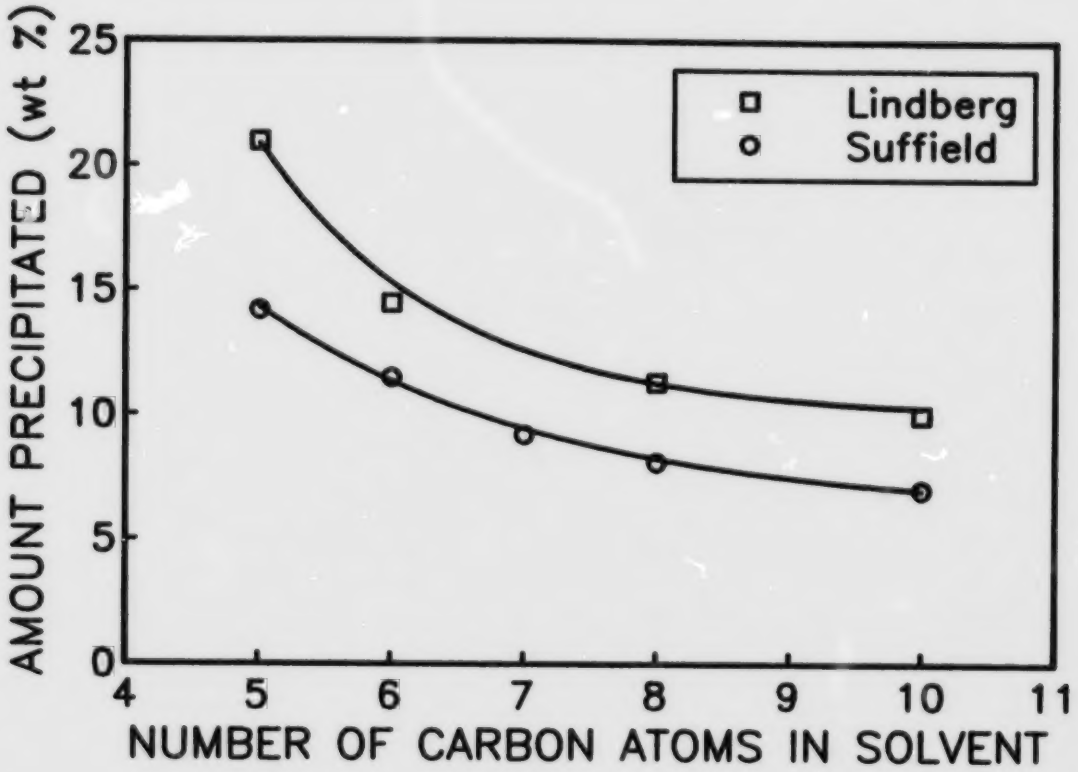
Wt % precipitate formed as a function of solvent ratio

FIGURE 27



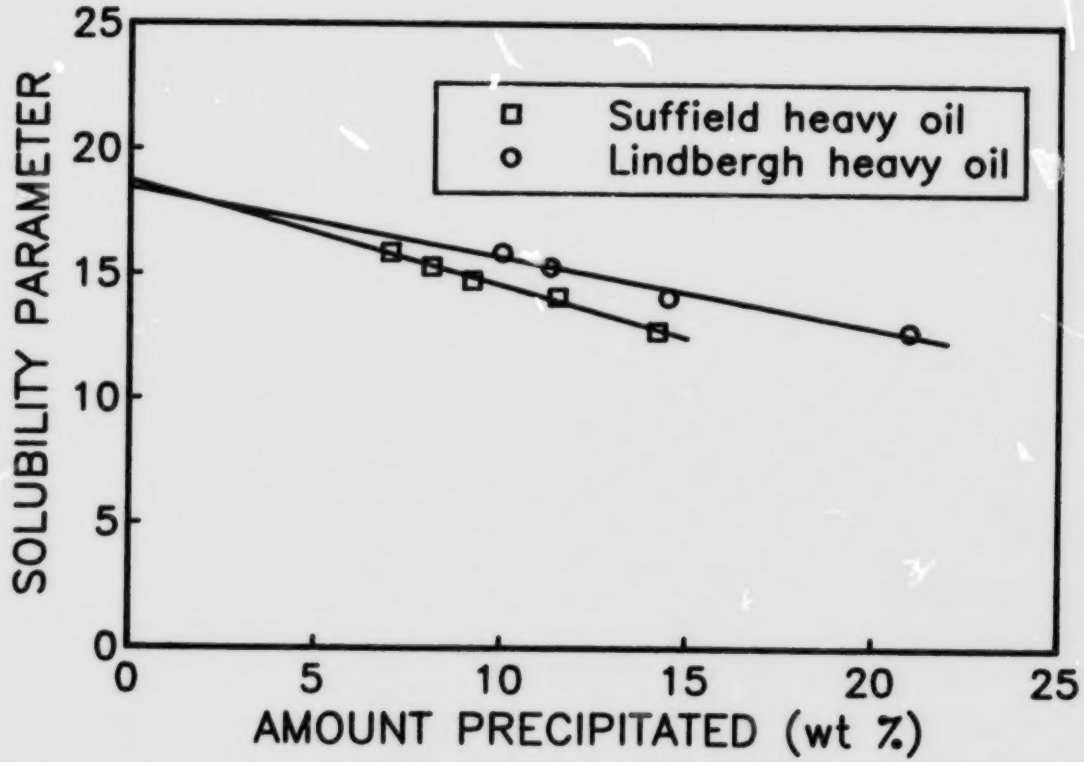
Wt % precipitate formed as a function of solvent ratio

FIGURE 28



Wt % precipitate formed as a function of carbon number in solvent

FIGURE 29



Relation of amount precipitated to solubility parameters of n-alkane solvents

FIGURE 30